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Sauer, Nancy N.

CATALYTIC REACTOR AND ORGANOMETALLIC MODEL STUDIES OF THE MECHANISM OF THIOPHENE HYDRODESULFURIZATION

Iowa State University PH.D. 1986

Catalytic reactor and organometallic model studies of the mechanism of thiophene hydrodesulfurization

by

Nancy N. Sauer

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DEDICATION

To my dad

SECTION I. HYDRODESULFURIZATION

GENERAL INTRODUCTION

Hydrodesulfurization, the process whereby sulfur is removed from crude oil or coal liquids is one of the most important processes in petroleum refining technology today.[1] In 1970, 10-15 million barrels of crude oil a day underwent hydrodesulfurization treatment, making it one of the largest chemical processes practiced.[2] This pretreatment of crude oils to convert the sulfur containing organic compounds to H_2S and hydrocarbons is necessary if they are to undergo further catalytic processing to fuels or petrochemicals. Reforming and hydrocracking catalysts, used initially to convert the raw materials to fuels, are particularly susceptible to poisoning and deactivation by sulfur.[1-3] Many of the catalysts for the production of petrochemicals also require low levels of sulfur in the reaction feed.

Figure 1.1 shows the most common sulfur containing compounds in petroleum. The thiols, disulfides, and sulfides are fairly readily desulfurized. The lower aromatic compounds however, are much more difficult to desulfurize, requiring higher temperatures and elevated hydrogen pressures. The desulfurization reaction for thiophene, a compound fairly typical of the aromatic species in petroleum, is shown in eqn. 1

(1)

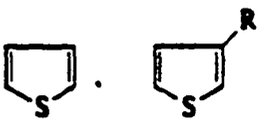
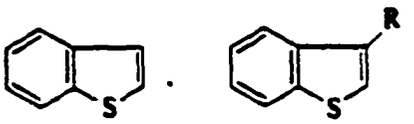
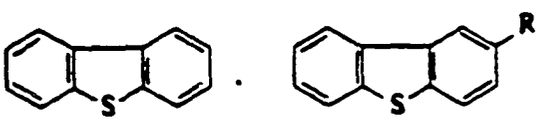
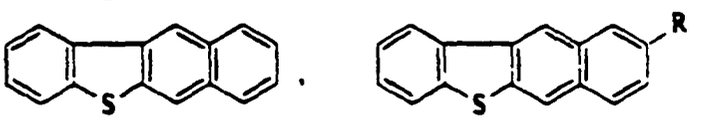
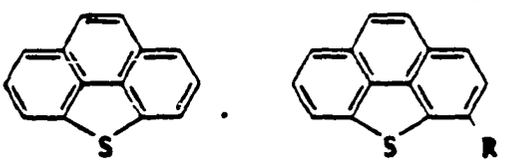
Compound class	Structure
Thiols (mercaptans)	RSH
Disulfides	RSSR'
Sulfides	RSR'
Thiophenes	
Benzothiophenes	
Dibenzothiophenes	
Benzonaphthothiophenes	
Benzo[*def*]dibenzothiophenes	

Figure 1.1. Common sulfur containing compounds in petroleum

Much of the petroleum refining in the United States today focuses on the production of fuels like gasoline, diesel or heating oil rather than petrochemicals. A major problem with the combustion of sulfur containing petroleum or coal derived fuels is the production of a major air pollutant, sulfur dioxide.[3] With the growing awareness of the environmental problems associated with sulfur dioxide, has come stricter pollution control standards which require drastic reductions in the sulfur content of fuels.

In direct conflict with these efforts is the realization that with the dwindling supplies of fossil fuels, lower grade, higher boiling, and more difficult to desulfurize crude oils and alternative energy sources like coal, must be used to meet current and anticipated energy demands. The sulfur content of these oils may be as high as 5-10%.[4] While rising costs and shortages of fuel have made processing of lower grade crude oils more economically attractive more efficient HDS processing will be necessary to adequately remove the sulfur.

Currently, removal of sulfur is accomplished over a supported, sulfided catalyst of cobalt-molybdenum, nickel-molybdenum, or nickel-tungsten. Generally, these catalysts are quite complex, with the nature of the active phase being widely disputed.[5] In part, the dispute is caused by the difficulty in obtaining detailed structural information about the catalyst surface. Only recently have spectroscopic techniques such as EXAFS, insitu raman and infra-red, EPS, and Mossbauer spectroscopies been applied to the study of the active phase of the catalyst. The development of these techniques,

along with the desire to develop superior new catalysts has lead to a tremendous surge of research in the area of HDS catalysis.

The section that follows contains a review of some of the more recent studies on HDS catalysts. In these studies, the researchers have attempted, by studying the sulfided, reduced catalysts, to gain information about the active surface site(s) on the catalyst. A complete discussion of all the literature on HDS catalysts is beyond the scope of this work. However, a number of excellent reviews detailing the work in this area have been published.[3,6]

THE CATALYSTS

The older catalysts used for hydrodesulfurization by industry were molybdenum or tungsten oxides supported on high surface area carriers like alumina.[6c] Reaction of the "oxide" form of the catalyst with H_2S in H_2, or with the sulfur containing-feedstock causes sulfiding and reduction to the active form of the catalyst.[5] Addition of cobalt or nickel to sulfided metal catalysts was found to lead to greatly enhanced activity; most HDS catalysts in industry contain these metals, commonly referred to as promoters. Both the sulfided Mo/Al_2O_3, and $Co\text{-}Mo/Al_2O_3$ catalysts have been used in studies to characterize the active form of the catalyts.

Molybdenum in HDS catalysts is thought to be present primarily as MoS_2.[7] Molybdenum disulfide has been detected on the sulfided catalysts by a variety of techniques, either as a layered structure as in bulk MoS_2, or as a distorted layer form.[5,8] Kwart and Schuit originally suggested the "monolayer" model where oxygen in the molybdenum layer is partly replaced by sulfur on sulfiding of the catalysts, giving a monolayer of MoS_2 on the catalysts.[9,10] Catalyst vacancies generated by reduction and sulfiding were designated as the active sites. Recent surface studies by Schrader,[8a,c] Topsøe,[11] Grimbalt,[12] and their coworkers, also suggest that the number of MoS_2 layers of the catalyst surface are quite low.

The crucial role of promoters in HDS catalysts is not understood as well.[5] A number of theories about how promoters affect catalysts have been suggested.[6a] Schuit has proposed that cobalt takes up edge positions in the layers of MoS_2, which results in an increase in the concentration of Mo^{3+}, which is believed to be the active site of the catalyst.[13] DeBeer et al. proposes that cobalt causes the breakup of large crystallites of MoS_2, increasing catalyst surface area.[14] Schrader and Cheung have shown that increased rates of reduction result when cobalt promoters are present.[8c] This inhibits the formation of bulk MoS_2. It has been suggested by Delmon that Co increases the dissociation of H_2, which spills over to the active sites in MoS_2, thus directly affecting ongoing HDS reactions.[15] The promotional effect of Co is also attributed to its increased hydrogenation ability, which would help prevents the buildup of deactivating coke deposits on the catalyst.[16]

Several different ideas have been put forth about the location of the promotor atoms in the catalyst substructure. In the intercalation model, molybdenum forms microcrystals of MoS_2 upon sulfiding. These microcrystals, which maintain the layer structure of large crystals, incorporate the cobalt promoter atoms between the double layers of sulfur.[13] Originally, Voorhoeve and Stuiver suggested that this intercalation occurred in Ni-W systems.[17] Farragher and Cosse in a modification of this model propose that the intercalation occurs at the edges of the MoS_2 domains.[18] The promoter function of the Co results from the increase in the number of Mo^{3+} sites at the crystal

edges. Other researchers have detected Co_9S_8 on sulfided catalysts, and maintain that it is the synergistic interaction of it with the MoS_2 which causes the promotional effect.[19] The Contact-Synergism model, as it is called, however does not seem to best describe the active sites; HDS activity was not found to correlate with the amounts of Co_9S_8 present on catalyst surfaces.[20]

More recently, in-situ Mossbauer studies have provided evidence for a new cobalt-containing phase, described as "Co-Mo-S".[21] The cobalt is believed to be substituted into the MoS_2 structure for molybdenum at the crystal edges.[22] This active phase has also been reported on silica- and carbon-supported catalysts.[23] A linear correlation between the amount of the Co-Mo-S phase present and catalyst HDS activity has been observed.[20]

The need to process heavier petroleum residues has led to a tremendous increase in the research being done on HDS catalyst preparation and characterization. Despite this accelerated research on HDS, many fundamental questions about the hydrodesulfurization process remain unclear. A review and discussion of the literature on the mechanism of HDS for thiophene will be presented in the following section.

PROPOSED MECHANISMS FOR THIOPHENE HDS

Because of the complex nature of crude oils, and the large variety of sulfur-containing compounds in them, many of the studies designed to probe the mechanism of HDS have been done with a model compound, thiophene. Thiophene is typical of the more difficultly desulfurized aromatic sulfur-containing compounds in most petroleum fuels. Numerous mechanisms and reaction schemes have been proposed for the HDS of thiophene, with both the initial bonding mode to the catalyst surface and the nature of the first step in the HDS process disputed. Much of the literature in this area is contradictory. The most widely discussed binding mode for thiophene is the "one point" binding mode, where only the sulfur directly interacts with the catalyst surface.[9] While much of the earlier literature assumes this type of surface attachment, more recent research however, has led to a multipoint adsorption scheme. Once bound, thiophene desulfurization is proposed to occur either by initial hydrogenation or through direct C-S bond cleavage. The following section details the proposed mechanisms for thiophene HDS and the experimental observations upon which the mechanisms are based.

Mechanisms with C-S Bond Cleavage as the Initial Step

Amberg mechanism

In the early 1960s Amberg and Owens published a series of papers on the HDS of thiophene over chromia/Al_2O_3 and CoMo/Al_2O_3 catalysts.[24] Their kinetic data and product distribution studies form the basis for the reaction pathway shown in Figure 1.2. At low hydrogen pressures and low conversions, they detected small amounts of 1,3-butadiene in the desulfurized products from the reaction of thiophene over chromia. While none was observed for the molybdenum catalysts, butadiene was assumed to be an intermediate as well. No tetrahydrothiophene, (THT), or butanethiol were seen as products over any of the catalysts in their reactor studies. Amberg's interpetation of these results was that the desulfurization step was not preceeded by ring hydrogenation, but the reaction went directly by hydrogenolysis of the carbon-sulfur bond.

Analysis of the desulfurized products, butane, 1-butene, and cis and trans 2-butene, showed that 1-butene was in excess of expected equilibrium amounts. From this and hydrogenation and isomerization studies of the butenes, it was concluded that the initial desulfurization step to give 1,3-butadiene was followed by rapid surface hydrogenation to produce 1-butene. Then, isomerization or hydrogenation of the 1-butene produced the observed product distribution.

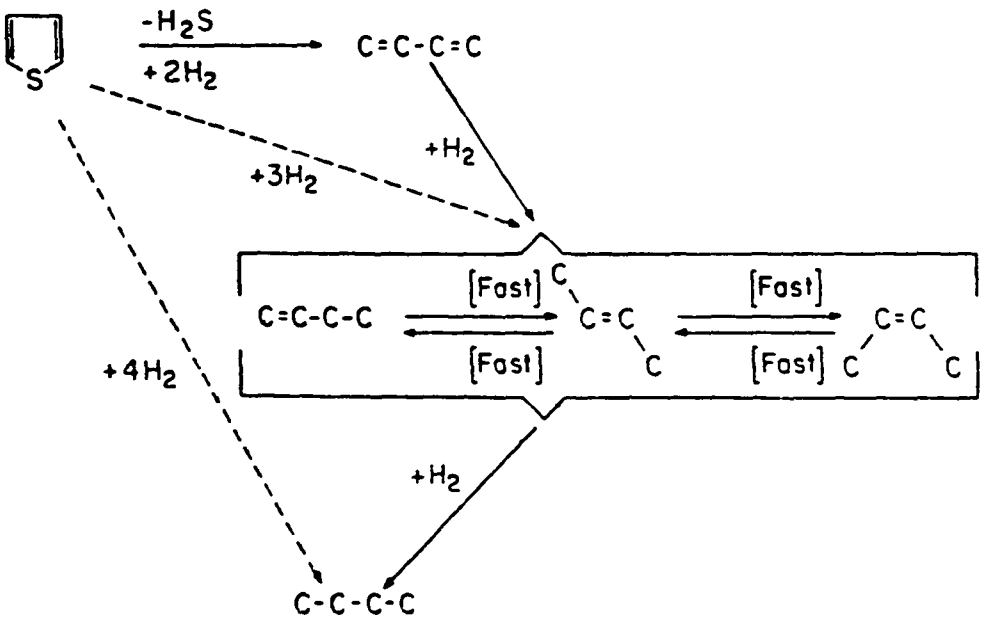


Figure 1.2. Amberg Mechanism

In an extension of these investigations, Desikan and Amberg examined the hydrodesulfurization of hydrogenated thiophenes, 2,3-dihydrothiophene,(2,3-DHT) and tetrahydrothiophene (THT)[25a] as well as 2 and 3-methylthiophenes.[25b] With the substituted thiophenes, they hoped to gain insight into the mechanism of the hydrogenolysis of the carbon sulfur bond. They observed that 3-methylthiophene was more reactive than both 2-methylthiophene and thiophene, implying that hydrogen chemisorption was not the rate determing step in the reaction. If it were, changes in the substrate structure should not have affected the rate of reaction. Heats of chemisorption for the 2 and 3-methylthiophenes were nearly the same, thus the differences in reactivity could not be explained on the basis of differences in the adsorption energy for the two substrates. Desikan and Amberg proposed instead, that the slow step in the HDS reaction is cleavage of the carbon sulfur bond. The surface species involved should be different for the thiophene and the two methylthiophenes, giving different rates of reaction. For this reason, they felt it unlikely that the reacting species was π bound to the catalyst through its aromatic ring.

In reactor experiments with THT and 2,3-DHT, Desikan and Amberg identified thiophene as a product. A reaction pathway which converted THT to thiophene, presumably through 2,3-DHT, had to exist. However, because of differences between the product distributions for thiophene and THT, and the fact that butanethiol was observed only for the desulfurization of hydrogenated thiophenes, Desikan and Amberg

concluded that the HDS of thiophene and THT proceeded by different routes. The reaction pathways for the hydrothiophenes and thiophene are shown in Figure 1.3.

Kolboe mechanism

Kolboe investigated the catalytic reactions of thiophene, tetrahydrothiophene and n-butanethiol over MoS_2, $CoMo/Al_2O_3$, and chromia catalysts.[26] Like Amberg and coworkers, Kolboe detected no organosulfur products at low hydrogen pressures and low conversions. He compared the product distributions from reactions using the three different sulfur compounds and saw that the amounts of butadiene formed from THT reaction exceeded that from thiophene over all three catalysts. From this he proposed that it was unlikely that thiophene and THT reacted through ring hydrogenation or dehydrogenation to give a single common type of surface intermediate which was then desulfurized to products. The beta elimination pathway, shown in figure 1.4 proposes that the initial step in the HDS reactions of these compounds is an intramolecular dehydrosulfurization. In this route, the carbon-sulfur bond cleavage is accompanied by transfer of a hydrogen from the carbons beta to the sulfur (step 1). For thiophene, the resultant surface intermediate is diacetylene, for THT, 1,3-butadiene. The adsorbed acetylene or butadiene were assumed to hydrogenate rapidly. The absence of diacetylene in the products of

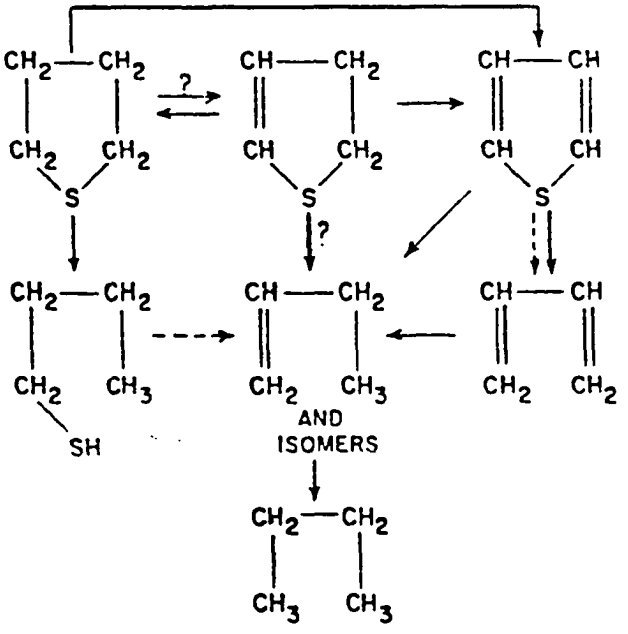


Figure 1.3. Amberg interconversion pathways for thiophene, 2,3-DHT, and tetrahydrothiophene

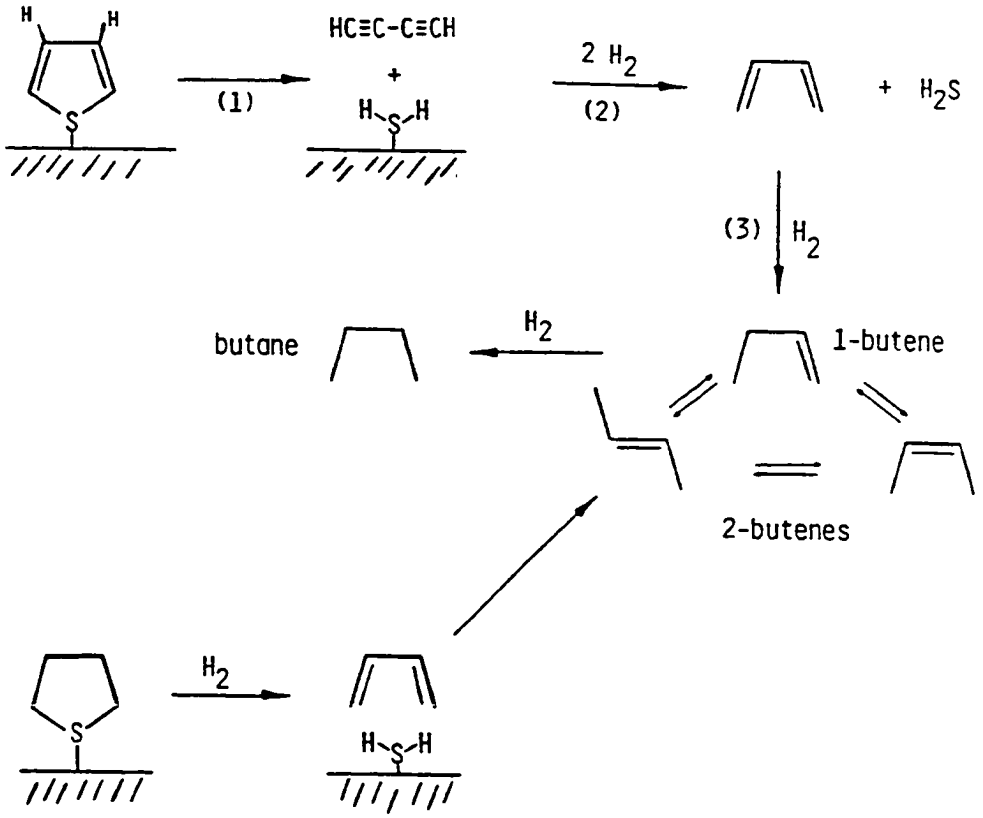


Figure 1.4. Kolboe desulfurization pathways for thiophene and tetrahydrothiophene

thiophene HDS was not inconsistent with the proposed mechanism. It is not unreasonable that a strongly bound surface diacetylene would undergo hydrogenation prior to desorption.

Kolboe's reaction scheme has received support from infra-red studies by Ratnasamy and Fripiat,[27] desulfurization studies of Mikovsky and Silvestri,[28] and very recently by work of McCarty and Schrader.[29] Infra-red experiments on the decomposition of thiophene over MoS_2 films showed a band at 3140-3160 cm^{-1}. This band, assigned to the asymmetric stretch of an acetylene supports the idea that thiophene decomposes through an acetylenic intermediate.[27] In experiments designed to distinguish between the Amberg and Kolboe mechanisms, Mikovsky et al. examined the deuterodesulfurization (DDS) of thiophene over a cobalt-promoted molybdenum catalyst. If desulfurization proceeded by an Amberg type of mechanism, primarily D_2S would be observed as the sulfur containing product. If the Kolboe mechanism was the path by which desulfurization occurred, then the products should contain H_2S. At low conversions Mikovsky et al. found little or no deuterium in the H_2S formed from the reaction. From this he concluded that the hydrogen for the desulfurization process must therefore come directly from the thiophene as the Kolboe mechanism would require, rather than from surface deuterium.

Similar results were observed by McCarty and Schrader in detailed DDS studies over a range of catalysts.[29] In this work, the isotopic content and deuterium distributions for thiophene, H_2S, butadienes and butenes were reported. These researchers found almost no deuterium in

hydrogen sulfide formed at conversions of 4%. They point out, however, that these results are also consistent with an earlier suggestion that surface exchange processes are responsible for large quantities of surface hydrogen. Thus, even if HDS proceeded by the Amberg mechanism, H_2S rather than D_2S would be formed.

Other evidence exists which is inconsistent with the Kolboe mechanism. Zdrazil[30] points out that the beta elimination mechanism, invoking a diacetylene intermediate, would be in contradiction with the products observed from the HDS of 3-methylthiophene, isopentanes and isopentenes. In addition, desulfurization of benzothiophenes by this pathway would require high energy benzyne intermediates. At the very least, another mechanism for HDS in these systems must exist.

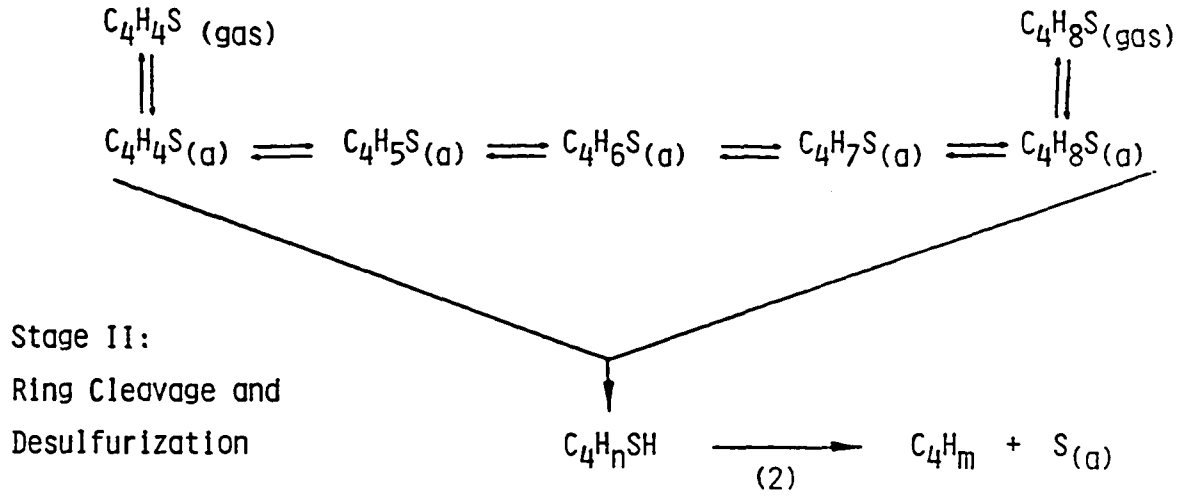
Mechanisms Involving Initial Hydrogenation of Thiophene

Kieran & Kemball Mechanism

In contrast to the results of Amberg and Kolboe, Kieran and Kemball,[31] Devanneaux and Maurin,[32] and Zdrazil,[30] all observed THT as a reaction product for thiophene HDS. Kieran and Kemball investigated reactivity of thiophene, THT and straight chain thiols over MoS_2 and WS_2. Reactivity comparisons indicate that straight chain molecules are much more readily desulfurized than cyclic molecules. The aromatic thiophene was the least reactive compound studied.

With these studies as a basis, they propose a complex reaction scheme for desulfurization which invokes hydrogenated surface intermediates. Two important observations support the proposed hydrogenated intermediates. The first was that they detected THT as a product of thiophene HDS. The second, that more butadiene was detected in the products of the desulfurization of THT than for thiophene. This second point refutes the claim that butadiene as a product in HDS reactions proves that C-S cleavage must occur prior to ring hydrogenation. The reaction mechanism proposed by Kieran and Kemball is broken into three stages, figure 1.5. In the initial stage, thiophene undergoes hydrogenation, establishing a surface equilibrium with a dihydrothiophene and THT. Direct desulfurization of THT is not, however, the suggested path that the thiophene HDS reaction takes. Instead, the partially hydrogenated intermediates are proposed to be activated for desulfurization. In stage II, rupture of a carbon sulfur bond occurs, and a straight chain thiol is formed. This is thought to be the rate determining step. The absence of thiols in the product stream is not taken as contradictory to the proposed scheme, as it is well established that thiols of this type are rapidly desulfurized over HDS catalysts. If step 2 is sufficiently rapid, little desorption of the intermediate thiol would occur. Hydrogenation and isomerization and subsequent desorption of the C_4 products occurs in the third stage.

Stage I: Hydrogenation of the Thiophene ring



Stage III: Isomerization and Desorption of Desulfurized Products

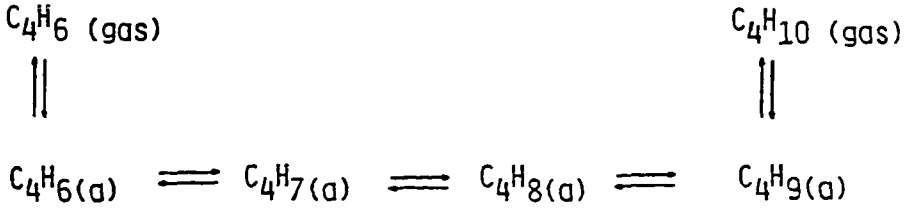


Figure 1.5. Pathway for thiophene hydrodesulfurization proposed by Kieran & Kemball. (g) indicates gas phase species; (a) indicates a surface adsorbed species

Dual Path Mechanism

The discrepancies between these results and those of Amberg and Kolboe, prompted Devanneaux and Maurin[32] to study thiophene and benzothiophene HDS over cobalt promoted moybdenum catalysts. The Deavanneaux-Maurin studies were done using higher hydrogen partial pressures, in the range of commercial HDS processes. In these studies, as with the earlier ones, the principal reaction products were butenes and H_2S. The detection of THT as a product led Devanneaux and Maurin to propose a two path mechanism (see figure 1.6), whereby thiophene could react by hydrogenation to give THT, which would subsequently desulfurize, or through carbon-sulfur bond hydrogenolysis as in the Amberg mechanism. Kinetic analysis of both the thiophene and benzothiophene data support this two path scheme, indicating two different catalytic sites, one for hydrogenation and one for C-S bond scission. Desikan and Amberg, who observed that pyridine inhibits the hydrogenation activity of the catalyst much more than the hydrodesulfurization ability also suggested that two different catalytic sites existed.[25]

In support of mechanisms involving hydrogenated surface species, Zdrazil found from the examination of C-S bond strengths, that direct cleavage of the aromatic C-S bond in thiophene would be difficult. Disruption of the aromatic resonance energy of the ring by hydrogenation destroys the double bond character of the C-S bond, making ring cleavage much more likely.[30]

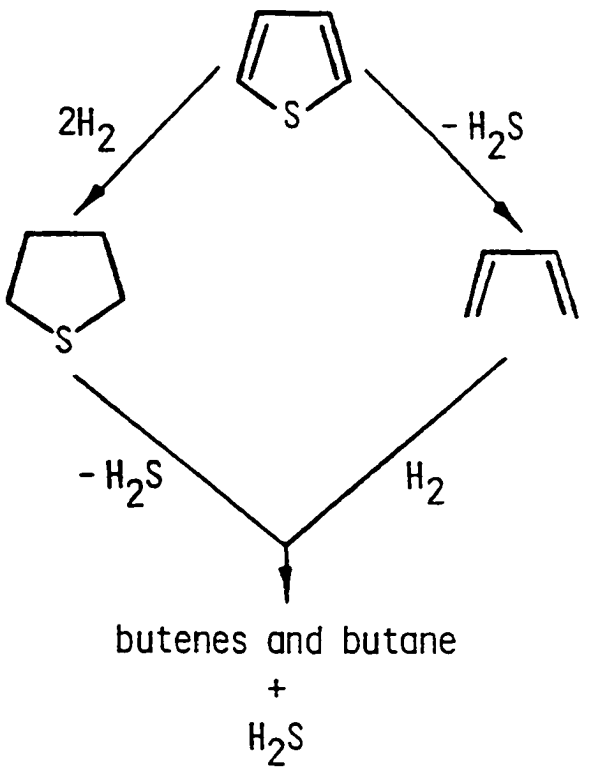


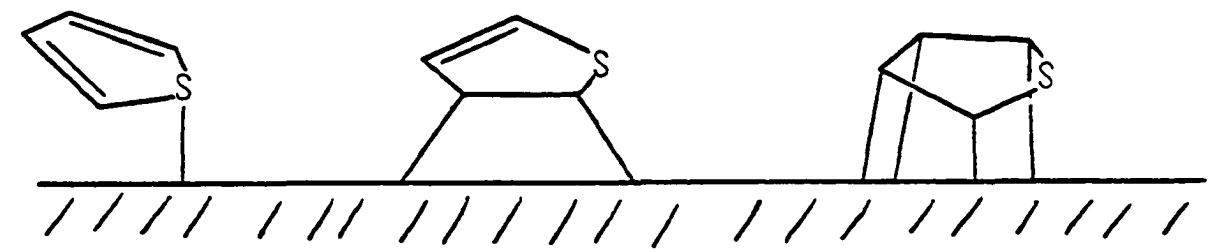
Figure 1.6. Dual Path Mechanism from the work of Devanneaux and Maurin

Full Mechanisms

The One Point Mechanism

In 1969, Lipsch and Schuit described reactivity and adsorption studies of thiophene over a Co-Mo/Al_2O_3 catalyst.[9] These results along with those of Amberg and coworkers,[24,25] Kolboe,[26] and Nickolson,[33] were used as the basis for the "One Point" mechanism for thiophene desulfurization. This mechanism, which puts forth a detailed description of the binding mode, active site and the mechanistic steps in the desulfurization of thiophene, postulates that thiophene binding to the catalyst occurs only through the lone pair of its sulfur. Earlier, Nickolson[33] reported infra-red data that showed three binding modes for thiophene, a one point-sulfur bound mode, a two point mode, and a multipoint mode where all of the thiophene carbon atoms interact with the catalyst surface, figure 1.7. The thiophene adsorbed through all four carbons was interpeted to be the active intermediate in HDS. Lipsch and Schuit reinterpeted these data and instead propose the sulfur bound species as the reactive intermediate.

The Lispch and Schuit mechanism, shown in figure 1.8 is also based on their investigations on the active form of the catalyst. They determined that reduction of the original supported MoO_3 not presulfiding as earlier suggested, was necessary for catalytic activity. Consistent with this is their proposed model where the sulfur interacts with the surface at an anion vacancy made available



One-Point Binding Mode | Two-Point Binding mode | Multipoint Binding Mode

Figure 1.7. Proposed binding modes for thiophene to the catalyst surface as suggested by Nickolson

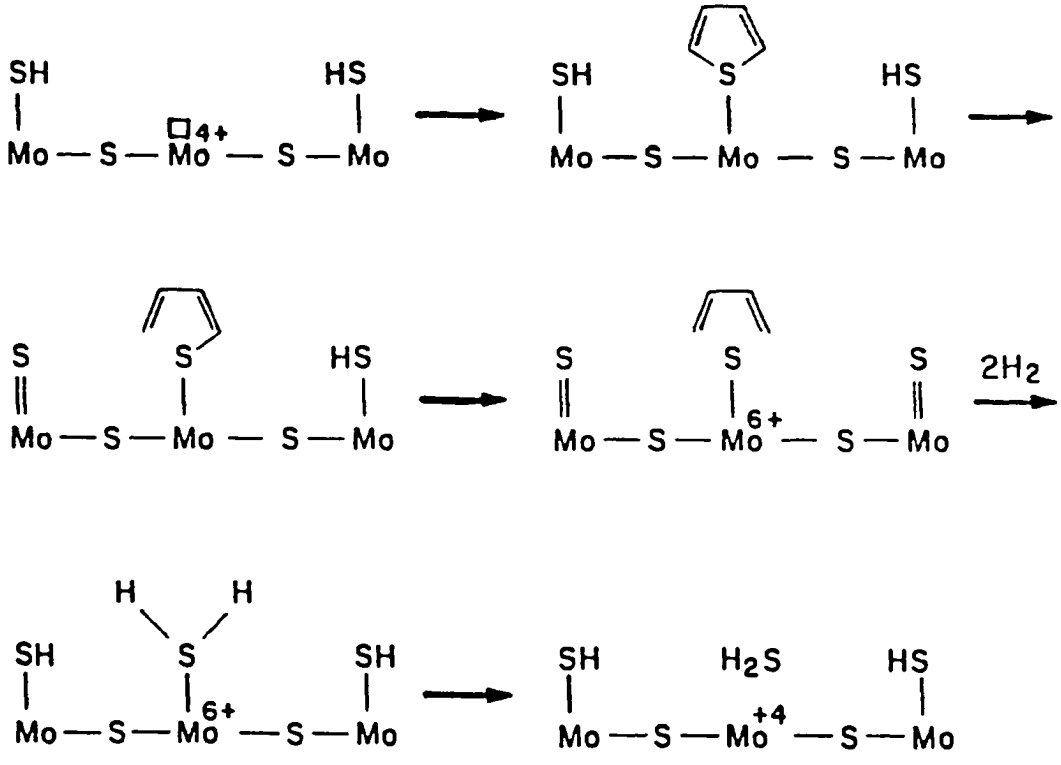


Figure 1.8. One Point Mechanism proposed by Lipsch and Schuit

by catalyst sulfiding and reduction. Surface attachment of this type was thought to assist the desulfurization process by weakening the carbon to sulfur bond; subsequent carbon sulfur bond cleavage gives butadiene as the initial desulfurization product. Butadiene either desorbs or is hydrogenated, and the catalytic site is regenerated by reaction with hydrogen to give H_2S.

While the one-point model asserts that thiophene adsorbs to the catalyst surface via a sulfur lone pair, several recent studies using a variety of surface science techniques have provided evidence that this view of thiophene binding is not correct. Benzigar et al. examined adsorption and desulfurization of thiophene on clean and sulfided Ni(111) planes using reflection-adsorption infra-red spectroscopy.[34] Their data suggest that the thiophene ring adsorbs parallel or nearly parallel to the Ni surface at 273 C, as would be necessary for a pi bound mode. Low energy electron diffraction (LEED) studies by Edwards and coworkers over Ni(111) have been interpeted to mean that the thiophene ring binds parallel to the metal surface.[35] Thermal Desorption spectra (TDS) taken of thiophene over Cu(100) planes show that under low exposure, thiophene is weakly pi bound to the Cu.[36] While these techniques indicate that thiophene binds in a pi fashion over highly ordered metal surfaces, no studies with sulfided catalysts have been reported; thiophene binding could be different over HDS catalysts. Presumably, the interaction of the pi system of thiophene with the catalyst surface should be maximum for this flat binding mode as is the case for benzene and alkyl

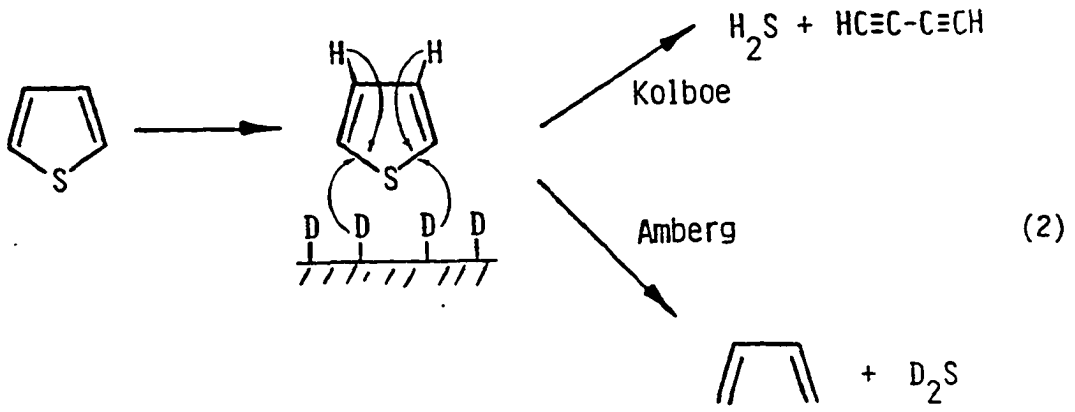
benzenes.[37] In a comparative adsorption study on Co-Mo/Al_2O_3 by Zdrazil,[38] adsorption by both the benzenes and thiophenic compounds was found to be quite similar.

The Cowley Mechanism

In 1977, Cowley described the deuterodesulfurization of 2,5-dideuterothiophene.[39] His studies focused on differentiating between the Amberg and β-elimination mechanisms. As described earlier, Mikovsky's observation of H_2S rather than D_2S as the sulfur containing product of the deuterodesulfurization of thiophene seemed to support formation of a diacetylene as the first step in the HDS process.[28] Cowley noted that for all the experiments done by Mikovsky, only 5% of the thiophene had undergone HDS, while 100% had undergone H/D exchange of the hydrogens. He reasoned that this would leave large quantities of protium on the catalyst surface near the thiophene binding site, which would cause H_2S to be produced upon sulfur elimination if desulfurization occurred by the Amberg mechansim. Because of this, he concluded that Mikovsky's results were consistent with both mechanisms.

In Cowley's studies, where the hydrogens of the 2 and 5 positions of thiophene were replaced with deuterium; exchange reactions occurring with the surface would not effect the amount of protium or deuterium in the product (H_2S or D_2S). If the Kolboe mechanism were operating, the protium in the beta positions of thiophene would still cause H_2S to be the product on sulfur elimination. However, if the

Amberg mechanism were the route by which desulfurization occurred, D_2S would be the detected product, rxn 2. Cowley observed large



(2)

quantities of D_2S (44%), and DSH (39%) being formed in his reactor studies, and concluded that the Kolboe pathway was not the route to desulfurization.

Cowley proposed a mechanism based on these deuterodesulfurization results as well as the observed exchange of thiophene and methylthiophenes at the alpha positions. Cowley's mechanism involved an unprecedented initial π adsorption mode for thiophene to the catalyst surface, with subsequent conversion to a sigma complex, Figure 1.9. He postulated that formation of a π complex allows the pi system of thiophene to share the large positive charge on the molybdenum, giving a strongly bound surface species. Cowley contended that this caused disruption of the aromaticity of the ring, making the C-S bond susceptible to cleavage. The sulfur associates with surface hydrogen in successive steps to give butadiene and H_2S as initial HDS products.

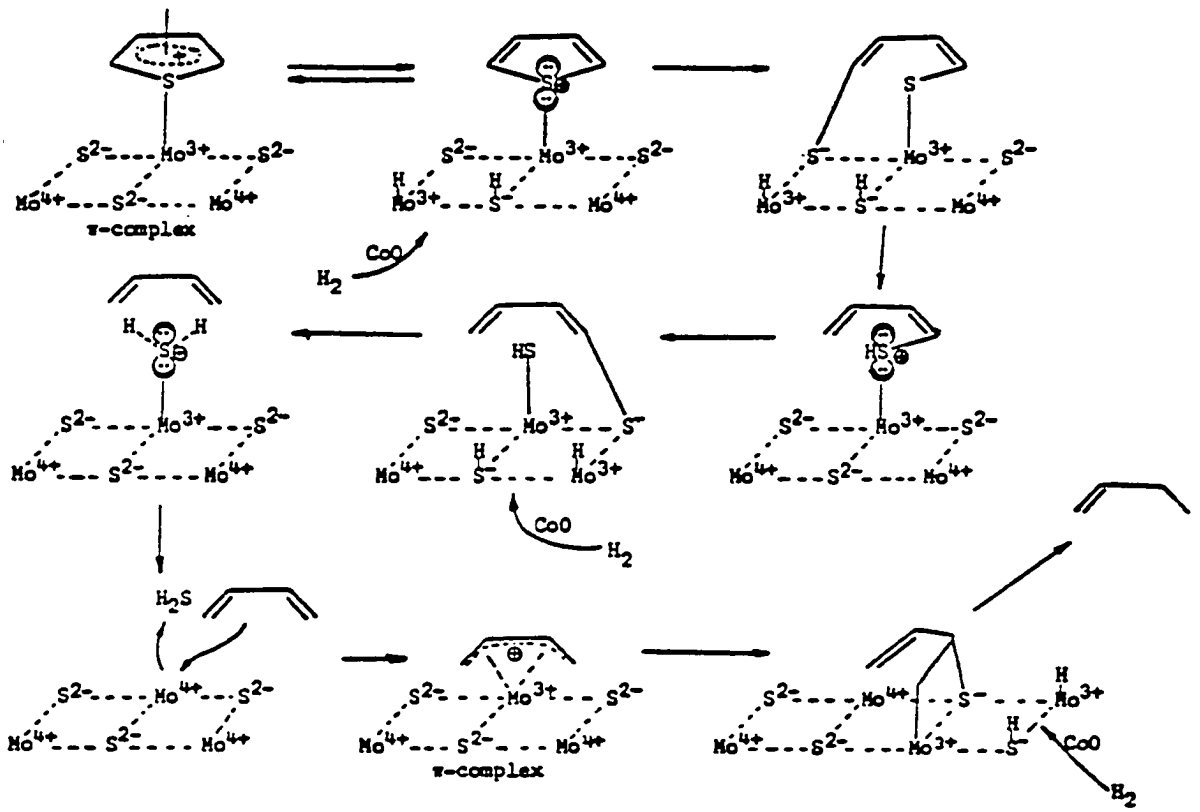


Figure 1.9. Cowley Mechanism

Cowley sites the exchange reactions of 2,5-dimethylthiophene as evidence for an initial pi thiophene. In this compound both the methyl hydrogens and the hydrogens in the 3 and 4 positions are beta to the sulfur. Random amounts of hydrogen were exchanged for deuterium under D_2 over the catalyst. Cowley reasoned from this that the activation energy for exchange must similar for all the hydrogens. This would be true for a π bound intermediate, but not true for a S-bound sulfur species.

In addition to Cowley's work, other evidence exists to refute the "one point" bonding model. Specifically, studies which examine the steric effects of thiophene binding. If thiophenes bind to the catalyst through the sulfur, substituents such as methyl groups adjacent to sulfur whould substanitally affect thiophene binding hence HDS reactions. However, Desikan and Amberg have shown that 2 and 3-methylthiophene undergo HDS over $CoMo/Al_2O_3$ with indistinguishable activation energies. This would not be expected for S-bound thiophenes.[25] Kinetic studies by Givens and Venuto with substituted dibenzothiophenes were carried out to determine the effect of beta substitution on the HDS reactivity.[40] At 300° C, and 100 atm H_2, 4,6-dimethyldibenzothiophene is 10 times less reactive than dibenzothiophene, but only two times less reactive that 4 methylbenzothiophene. A much larger difference would be expected if the dibenzothiophene coordinated to the surface through its sulfur.

The Multipoint Model

Kwart, Schuit, and Gates reviewed the inconsistencies in the one point mechanism, and proposed instead a model whereby thiophene is adsorbed at an anion vacancy in the catalyst through a single pi bond.[41] In support of this mechanism, they cite Daudel et al, who estimated the partial double bond character of the bonds in thiophene.[42] The C_1-C_2 bond has the highest electron density, hence they suggest that adsorption to the catalyst surface would preferentially occur through this bond. Their detailed proposal is shown in figure 1.10. In such a bonding mode, the thiophene sulfur atom would be positioned to interact with a neighboring surface sulfur atom. Coordination of the pi bond causes the sulfur to become electron deficient promoting its bonding to a surface sulfur. Simultaneous addition of hydrogen to C_1 and C_2 would result in a coordinated 2,3-dihydrothiophene type intermediate. This species could readily undergo beta elimination as in step E because it no longer has aromatic stabilization. Repetition of either of these steps would give a surface bound butadiene which would react further to give the observed products of the HDS reaction.

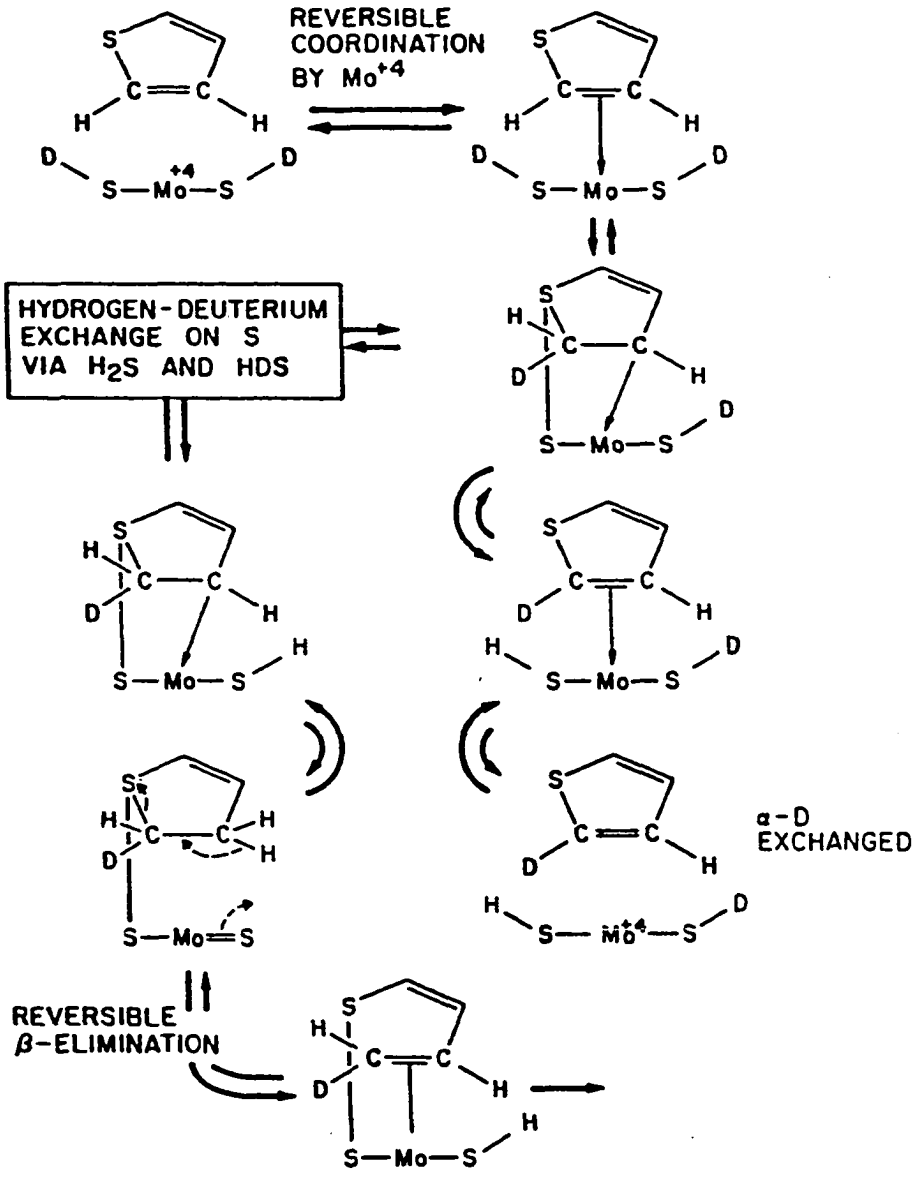
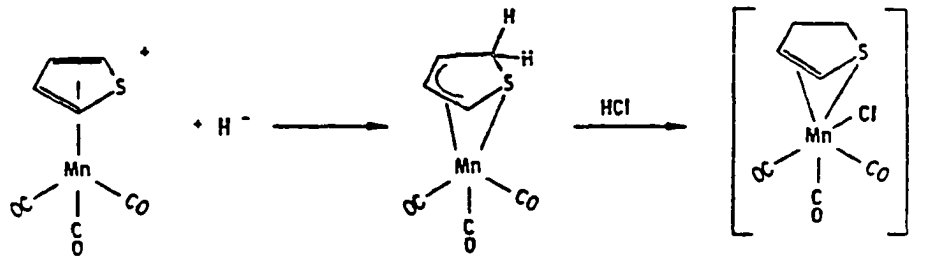


Figure 1.10. Multipoint Mechanism proposed by Kwart, Schuit, and Gates

ORGANOMETALLIC MODELS FOR THIOPHENE HDS

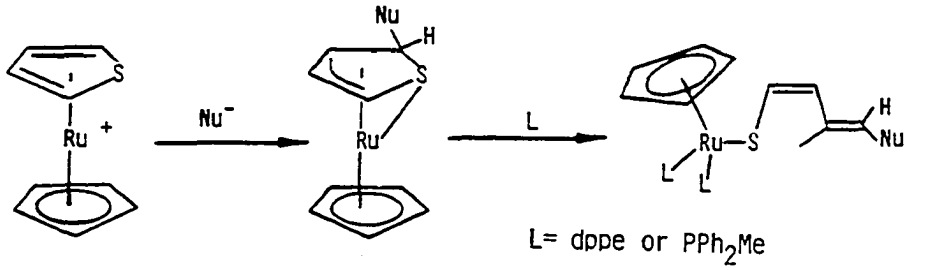
Thiophene exhibits two binding modes to transition metals, an S-bound mode, and a pi bound mode, where the full aromatic ring of the thiophene is coordinated to the transition metal as in π-benzene complexes. There are just three reasonably well characterized thiophene complexes of the S bound type, $Ru(NH_3)_5(SC_4H_4)$,[43] $Cp(CO)_2Fe(SC_4H_4)$,[44] and $[(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)]BPh_4$.[45] At best, the thiophene in these complexes is weakly bound, being readily displaced by other donor ligands. Perhaps because of this, no reactivity studies of the thiophene in these complexes have been reported. In contrast, a number of compounds with coordinated π thiophene are known and are quite stable. Recent reactivity studies with several of these complexes show that the thiophene is quite activated to undergo reactions of the type seen over the catalyst surface.[46]

The complex $[Mn(CO)_3(\eta\text{-thiophene})]$ has been shown to undergo attack with a variety of nucleophiles, ($Nu=CN^-, OMe^-, C_6H_5^-, H^-$, and $P(n\text{-}Bu)_3$.[46d] The resultant allyl sulfide product can be protonated with HCl giving an unstable 2,3-dihydrothiophene complex, eqn. 3. The exact formulation of the 2,3-DHT compounds, monomer or dimer, is not definitively known. The thiophene ring in the analogous 2-methylthiophene derivative has been shown to be activated as well.



(3)

Reaction of thiophenes with $[CpRu(NCMe)_3]BF_4$ gives the complexes $[CpRu(\eta\text{-thiophene})]BF_4$, where thiophene is thiophene, 2-methylthiophene or 2,5-dimethylthiophene. The thiophene and 2-methylthiophene complexes react with nucleophiles like MeO^-, MeS^-, EtS^-, and $iPrS^-$ to give allyl sulfide adducts of the type observed in the manganese thiophene system. Reaction of the adducts with excess phosphine, PMe_3, PPh_2Me and dppe, result in the formation of ring opened butadienethiolato compounds, eqn. 4. In addition to these reactions, the thiophene complex, $[CpRu(\eta\text{-thiophene})]BF_4$ has also been shown to undergo base promoted deuterium exchange, modeling the observed exchange over HDS catalysts.



(4)

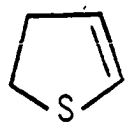
L= dppe or PPh_2Me

STATEMENT OF PROBLEM

The inconsistencies and contradictions in the HDS literature for thiophene make definitive conclusions about a detailed mechanism for removal of sulfur from thiophene impossible. The need for a better understanding of the basic steps in hydrodesulfurization is clear. Quite possibly, several different pathways for desulfurization exist and are in operation on catalyt surfaces; the predominate paths determined by specific catalysts and reaction conditions. Features of the mechanism for thiophene which need to be detailed include the binding mode to the catalyst surface and the pathways available for desulfurization. The goal of this research was to address these questions through a two-fold approach; heterogeneous reactor studies using proposed HDS intermediates as reactor feeds, and through organometallic modelling of thiophene binding and reactivity on HDS catalysts.

Reactor Studies

With recent work at near industrial conditions implicating hydrogenated intermediates in this process, we choose to examine the reactivities of 2,3 and 2,5-dihydrothiophene (figure 1.11) over a supported rhenium catalyst. The distributions of products for these reactions were compared to the products seen for thiophene HDS under the same conditions. Deuterodesulfurization studies were used to



2,3-Dihydrothiophene

2,5-Dihydrothiophene

Figure 1.11. The dihydrothiophenes

investigate the route by which the observed products were formed. Only one catalytic study using either of the dihydrothiophenes as a reactor feed has been reported in the literature.[25b]

Organometallic Model Studies

Organometallic compounds have been shown to be helpful in modeling short-lived surface intermediates in several catalytic systems.[47] Because complexes can be isolated and completely characterized, they can be studied in far more detail than species on a catalyst surface. One area of HDS which was examined using model complexes was the deuterium exchange of thiophenes over HDS catalysts. Deuterium exchange occurs for thiophene and substituted thiophenes at low temperatures (200° C) when deuterium is used rather than hydrogen.[39,48] Ruthenium complexes containing pi bound thiophenes have been shown to undergo deuterium exchange in the presence of base in d_4-methanol.[46b] Kinetic studies of these systems

were done to determine relative rates of exchange of the hydrogens on the thiophene rings.

Model complexes with dihydrothiophene ligands were prepared as well. Specifically, the model reactions which were attempted were drawn from the observed reactivity of 2,3 and 2,5-DHT over the 5% Re/Al_2O_3 HDS catalyst used in the reactor studies. The final section of this thesis will contain details of the organometallic chemistry of 2,3-dihydrothiophene complexes such as variable temperature proton nmr studies, and attempts to prepare π-bound 2,3-DHT complexes.

In addition to the π bound mode observed by Lesch et al., 2,3-dihydrothiophene could be expected to bind to transition metals through one of the sulfur lone pairs, like a typical thioether. Because of the limited availability of this reactive compound, only one transition metal complexes with 2,3-dihydrothiophene as a ligand has been prepared; Eekhof et al. have described the preparation of $Cr(CO)_5SC_4H_6$. This complex, which was obtained by the photolysis of $Cr(CO)_6$ in a benzene solution containing the 2,3-DHT, was not further studied.[49]

EXPLANATION OF DISSERTATION FORMAT

This thesis is broken into five separate sections consisting of a general thesis introduction, followed by four sections representing thesis research as it was submitted for journal publication. Each of these sections is self-contained; literature citations and figures pertain only to the section that they are in. The final section of the thesis is a summary of the thesis work.

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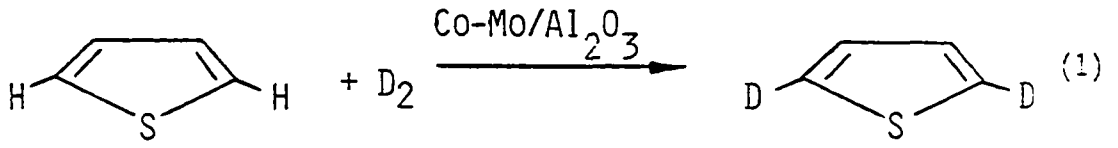
SECTION II. (η-THIOPHENE)Ru(η-C_5H_5)$^+$ AS A MODEL FOR THE ADSORPTION AND DEUTERIUM EXCHANGE OF THIOPHENES ON HYDRODESULFURIZATION CATALYSTS

INTRODUCTION

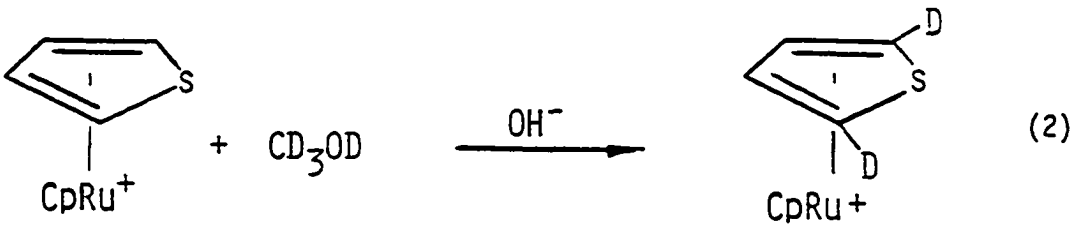
Catalytic removal of sulfur from organosulfur compounds in petroleum is accomplished industrially over a cobalt-promoted molybdenum catalyst at high temperatures and elevated H_2 pressures in a process known as hydrodesulfurization (HDS).[1,2] Despite a tremendous number of studies attempting to elucidate specific steps in this process, many key questions about the mechanism remain.[3] Thiophene, one of the sulfur-containing compounds which is most difficult to desulfurize, undergoes, prior to desulfurization, extensive exchange (eqn. 1) with deuterium on the catalyst if D_2 is used in the reaction. Exchange occurs primarily at the 2 and 5 (α)



(1)

positions of the ring with much smaller amounts being incorporated at the 3 and 4 (β) positions.[4] This exchange pattern has frequently been used as evidence to support the proposal that thiophene binds to HDS catalysts through an "end on" attachment, i.e., through its sulfur atom only.[4a,c] Presumably, such an adsorption mode would selectively activate the 2 and 5 hydrogens toward deuterium exchange by placing them in close proximity to the catalyst surface. However, recent studies designed to probe the surface attachment of thiophene to the catalyst surface suggest that a π bound adsorption mode is more

likely.[4d,5-6] Indeed, model studies have shown[7] that π-thiophene ligands in transition metal complexes are highly activated to undergo reactions analogous to those suggested to occur on the catalyst. Among these reactions is the rapid exchange[7c] of the hydrogens at the 2 and 5 positions of thiophene in [CpRu(thiophene)]BF_4, Cp = η-C_5H_5, in the presence of bases in d_4-methanol (eqn. 2); no exchange is observed at the 3 and 4 positions over short periods



(2)

of time (< 15 minutes). This complex was also found to exchange over Al_2O_3 which was deuterated with D_2O.[7c]

As for thiophene over HDS catalysts, methylthiophenes undergo more rapid exchange in the 2 and 5 positions than in the 3 and 4 positions; the least amount of exchange occurs in the CH_3 groups.[4a] For the purpose of comparing relative rates of deuterium exchange over heterogeneous catalysts with those of model complexes with π-bound thiophene ligands, we report herein kinetic studies of base-promoted deuterium exchange in [CpRu(thiophene)$^+$], where thiophene represents thiophene, 2-methylthiophene, 3-methylthiophene, and 2,5-dimethylthiophene. The relative rates of exchange which we observe strongly support π-bonded thiophenes as intermediates in their exchange with deuterium over HDS catalysts.

EXPERIMENTAL

General Procedures. Kinetic studies were performed on a Bruker WM-300 NMR spectrometer. All other ^{1}H NMR and ^{13}C NMR spectra were recorded on a Nicolet NT-300 spectrometer. Chemical shifts are referenced to internal $(CH_3)_4Si$ using deuterated solvents as internal locks. FAB mass spectra were obtained on a Kratos MS-50 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc. The thiophene complex [CpRu(thiophene)]PF_6, **1** was prepared as previously described.[7c] The 2- and 3-methylthiophenes (2-MT and 3-MT) and 2,5-dimethylthiophene (2,5-DMT) (Aldrich) were distilled over CaH_2 at ambient pressure before use. Methylene chloride and CH_3CN were distilled from CaH_2 and stored over 4 Å molecular sieves prior to use. Diethylether, acetone, and 1,2-dichloroethane were used without further purification. The standardized 0.50 M KOH in methanol solution was purchased from Aldrich and used without further purification. The 99.5% D CD_3OD was purchased from Norell Inc. and stored over 4 Å molecular sieves prior to use. Methanol was distilled from CaH_2 under N_2.

Preparations of [CpRu(η-2-MT)]BF_4 (2) and [CpRu(η-2,5-DMT)]BF_4 (4). Method I. The complex $CpRu(PPh_3)_2Cl$[8] (1.00 g, 1.38 mmol), $AgBF_4$ (0.290 g, 1.52 mmol), and 3 mL of 2-MT or 2,5-DMT were refluxed in 20 mL of CH_3OH for 24 h under N_2. Isolation of the product was accomplished by removing the volatiles from the reaction mixture <u>in vacuo</u>, extracting the residue with CH_2Cl_2, and precipitating the product from the filtered solution by slow addition of Et_2O.

Successive recrystallization from CH_2Cl_2/Et_2O yielded the salts as brown powders (yield: ca. 40% for both complexes). [CpRu(η-2-MT)]BF_4: ^1H NMR ($CDCl_3$): δ 5.39 (s, C_5H_5), 6.29 (m, H_3 and H_4), 6.13 (d, H_5), 2.42 (s, Me_2); ^{13}C NMR ($CDCl_3$): δ 80.93 (C_5H_5), 86.80, 86.18, 77.90 (C_{3-5}), 80.43 (C_2), 15.59 (Me); M.S. (FAB, glycerol): m/e 265 (M^+); Anal. Calcd for $C_{10}H_{11}BF_4RuS$: C, 34.21; H, 3.16; S, 9.13. Found: C, 34.32; H, 3.17; S, 8.93. [CpRu(η-2,5-DMT)]BF_4: ^1H NMR ($CDCl_3$): δ 5.35 (s, C_5H_5), 6.23 (s, $H_{3,4}$), 2.37 (s, Me); ^{13}C NMR ($CDCl_3$): δ 81.04 (C_5H_5), 86.89 ($C_{(3,4)}$), 82.38 ($C_{2,5}$), 15.77 (Me); M.S. (FAB, glycerol): m/e 279 (M^+); Anal. Calcd for $C_{11}H_{13}BF_4RuS$: C, 36.18; H, 3.59; S, 8.78; Found: C, 36.38; H, 3.64; S, 9.20.

Method II. As described by Gill and Mann,[9] [CpRu(η-C_6H_6)]PF_6 (0.552 g, 1.42 mmol) was photolyzed in 280 mL of CH_3CN to give [CpRu($NCCH_3$)$_3$]PF_6. The solvent was then removed in vacuo. The remaining oily solid was dissolved in 25 mL of $ClCH_2CH_2Cl$ containing 4 mL of 2-MT. After refluxing the solution for 16 h under N_2, the volatiles were removed in vacuo, and the residue was extracted with a minimum of warm acetone. After filtering off the insoluble material, the product was precipitated with Et_2O as a pale brown solid; yield, 0.348 g, 60%. The ^1H NMR spectrum of [CpRu(η-2-MT)]PF_6 was identical to that of [CpRu(η-2-MT)]BF_4 (2) prepared by method I.

[CpRu(η-C_6H_6)]BF_4, (0.260 g, 0.785 mmol), prepared as described by Gill and Mann,[9] for the PF_6^- salt using $[NH_4]BF_4$ instead, was photolyzed in 280 mL of CH_3CN. The solution containing [CpRu($NCCH_3$)$_3$]BF_4 was evaporated to dryness, and refluxed in 25 mL of

$ClCH_2CH_2Cl$ with 4 mL of 2,5-DMT for 16 h. The reaction mixture was worked up as described for [CpRu(η-2-MT)]BF_4, method II; yield 0.332 g, 60%. The ^1H NMR spectrum of the product was identical to that of [CpRu(η-2,5-DMT)]BF_4 (4) prepared by method I.

Preparation of [CpRu(η-3-MT)]BF_4 (3). Using method II, [CpRu(η-C_6H_6)]BF_4, (0.250 g, 0.753 mmol) was photolyzed in 280 mL of CH_3CN for 24 h. The CH_3CN was removed <u>in vacuo</u>, and the brown residue, [CpRu($NCCH_3$)$_3$]BF_4 was dissolved in 30 mL of $ClCH_2CH_2Cl$; 4 mL of 3-MT was added, and the mixture was refluxed for 24 h. The $ClCH_2CH_2Cl$ was removed under vacuum, and the brown solid was recrystallized from hot acetone/diethyl ether. Yield: 0.122 g, 0.35 mmol, 46%. ^1H NMR (d_6 acetone): δ 5.48 (s, Cp); 6.58 (d, J=2.96 Hz, H_5), 6.41 (s, H_2), 6.39 (d, J=2.96 Hz, H_4); ^{13}C NMR (acetone): δ 81.27 (C_5H_5); 88.46, 79.66, 79.24 ($C_{2,4,5}$), 69.14 (C_3), 14.75 (CH_3).

Kinetic Measurements. Rates of deuterium exchange into the thiophene complexes were measured by following the disappearance of the appropriate ^1H NMR peaks with time. Reactions of the thiophene complexes **1-4** with base were carried out under a N_2 atmosphere in NMR tubes sealed with rubber septa. The thiophene compound of interest was placed in the NMR tube under N_2 and the d_4-methanol was added by syringe. Samples were thermostated in the probe of the NMR spectrometer at 23 ± 1°C for 10 minutes; then the 0.50 M KOH/CH_3OH solution was added by microliter syringe to give the desired KOH concentration. The NMR tube was lowered back into the probe of the NMR, the NMR shimmed, and the data acquisition started. For a typical

sample, 4 minutes passed between the time the base was added and data collection was begun. For most samples, the disappearance of the thiophene protons was monitored by periodic integration against the Cp ring protons of the complex. For several samples, [CpRu(η-thiophene)] PF_6 (1) with 0.0150 M KOH and 0.0875 M KOH and [CpRu(η-2-MT)]PF_6 (2) with 0.50 M KOH, an internal standard of t-butanol was added. The Cp ring and exchanging H_3 and H_4 proton signals were integrated relative to the t-butanol. While the resonances for H_3 and H_4 decreased, no exchange of the Cp ring protons was observed. For the remaining samples, decrease of the H_3 and H_4 resonances was determined by integration against the Cp ring. Analysis of the exchange data was done using the McKay equation, which is also the equation for a pseudo first order reaction;[10,11] linear plots of ln(1-F) *vs.* t (F = the fraction of exchange which had occurred) give a slope, k_{obsd}. Values of (1-F) were obtained from the integrated area of the proton of interest, $F = (A_o - A_t)/A_o$, where A_o is the integrated area before base addition, and A_t is the area at time t. The rate constants, k_{obsd}, were obtained from least squares analysis of plots of ln (1-F) *vs.* t which were linear for at least 75% of the reaction. In all reactions, concentrations of CD_3OD were at least 50 times that of the thiophene compound. For all compounds, **1-4**, deuterium exchange of $H_{3,4}$ was observed to go to completion. Several of the free thiophenes were tested to see if they exchanged in the presence of base in CD_3OD. No exchange of 2- or 3-MT in 0.050 M KOH in CD_3OD was obsered over a period of 60 h. Likewise, no exchange of thiophene was seen in

0.35 M KOH in CD_3OD over 24 h.

Exchange Preparation of [CpRu(η-d_4-thiophene)]PF_6. [CpRu(η-thiophene)]PF_6, 1, (0.030 g, .076 mmol) was dissolved in dry degassed CH_3OD (20 mL), and 0.50 M KOH in CH_3OH (0.75 ml) was added by syringe. The solution was stirred for 8 h, at which time exchange of all 4 thiophene protons was observed to be complete by ^1H NMR. Gaseous CO_2 was bubbled through the solution for 1 h to neutralize the base, and the solvent was removed. The residue was extracted with a minimum of freshly distilled CH_2Cl_2, and the product was precipitated by addition of Et_2O. The product was recrystallized from CH_2Cl_2/Et_2O two more times. The [CpRu(η-d_4-thiophene)]PF_6 was identified by its ^1H NMR and mass spectra.

Based-Catalyzed Exchange of [CpRu(η-d_4-thiophene)]PF_6 with CH_3OH. [CpRu(η-thiophene)]PF_6, (0.025g, 0.063 mmol) was dissolved in CH_3OH (9 mL). The mixture was immersed in a constant temperature bath (25.0°) and 0.50 M KOH in CH_3OH (1 mL) was added by syringe. One-mL samples were removed at different times to monitor the exchange; the base in each sample was neutralized by bubbling CO_2 through the solution for 30 min, and the CH_3OH solvent was removed **in vacuo**. The residue was dissolved in d_6-acetone, and the ^1H NMR spectrum was taken. The extent of exchange was determined by integrating the thiophene proton signals of the product 1. Positions 2 and 5 exchanged completely within 10 min. The $H_{3,4}$ signals appeared much more slowly and were integrated relative to the $H_{2,5}$ peaks.

RESULTS

Rate constants, k_{obsd}, for the KOH-catalyzed deuterium exchange reactions, e.g., eqn. 3,

$$CpRu(SC_4H_4)^+ \xrightarrow[CD_3OD]{OH^-} CpRu(SC_4H_{4-x}D_x)^+ \quad \text{where } x = 1\text{-}4 \qquad (3)$$

of **1-4** with CD_3OD are given in Table I. As discussed below, detailed kinetic studies were possible only for the exchange of the $H_{3,4}$ protons. All reactions can be fit to the rate expression:

$$\frac{d[Ru]}{dt} = k[Ru][OH^-] = k_{obsd}[OH^-] \qquad (4)$$

where [Ru] represents the concentration of the complexes **1-4.** Values for the second order rate constants k (Table II) were obtained from slopes of plots of k_{obsd} *vs.* $[OH^-]$. In each of these plots, k_{obsd} had a small intercept value at $[OH^-]$ = 0.00 M. These small intercepts are probably within experimental error of zero. In fact, there was no measurable deuterium exchange of $H_{3,4}$ when [CpRu(η-thiophene)]BF_4 reacted with CD_3OD in the absence of KOH for 20 h; in the presence of the base concentrations used in the kinetic studies (Table I), the exchange of these protons was complete within 6 h.

In all complexes (**1-3**), deuterium exchange of the H_2 and H_5 protons was too fast to follow by our ^1H NMR method. Complexes **1-3** in the presence of 1.00×10^{-3} M KOH (> 60:1 ratio of complex: KOH), gave complete exchange of $H_{2,5}$ in less than 3 minutes. A lower limit on the rate constant, k, for this exchange was estimated (for $t_{\frac{1}{2}}$ = 90

Table I. k_{obsd} Rate Constants for KOH-Catalyzed Exchange of H_3 and H_4 in Complexes **1-4** in CD_3OD at 23°C

10^2[KOH], M	$10^4 k_{obsd}$, s^{-1}
[CpRu(η-thiophene)]PF_6 (1) (1.39 x 10^{-2}M)	
0.875	0.78
1.25	1.1
2.50	2.0
3.75	2.7
5.00	3.7
[CpRu(2-methylthiophene)]BF_4 (2) (3.13 x 10^{-2}M)	
1.50	0.43
2.50	0.69
5.00	1.1
7.50	1.5
8.75	1.8
[CpRu(3-methylthiophene)]BF_4 (3) (3.65 x 10^{-2}M)	
2.50	0.35
5.00	0.60
8.75	1.0
10.00	1.2
12.50	1.5
[CpRu(2,5-dimethylthiophene)]BF_4 (4) (3.02 x 10^{-2}M)	
8.75	0.35
10.00	0.42
12.50	0.63
16.00	0.75
20.00	0.99

Table II. Second Order Rate Constants, k, for Exchange of H_2 and H_5, H_3 and H_4, and CH_3 in Complexes **1-4** at 23°C in CD_3OD Solvent

H_2, H_5	$10^3k\ M^{-1}s^{-1}$
[CpRu(η-thiophene)]PF_6, (1)	> 1500
[CpRu(2-methylthiophene)]BF_4, (2)	> 1500
[CpRu(3-methylthiophene)]BF_4 (3)	> 1500
$H_{3,4}$	
[CpRu(η-thiophene)]PF_6, (1)	8.0
[CpRu(2-methylthiophene)]BF_4, (2)	2.4
[CpRu(3-methylthiophene)]BF_4, (3)	1.2
[CpRu(2,5-dimethylthiophene)]BF_4, (4)	0.45
CH_3	
[CpRu(2-methylthiophene)]BF_4, (2)	0.20

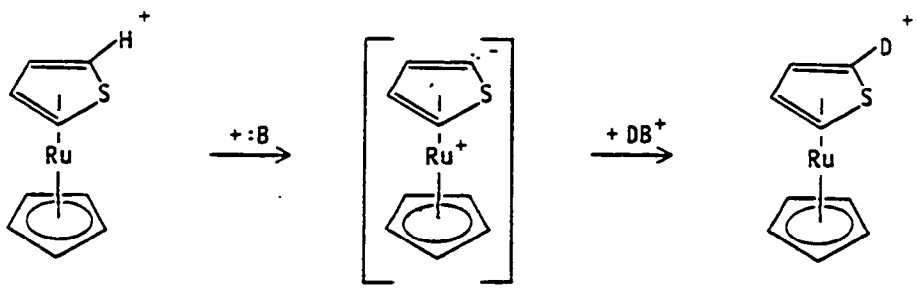
sec, $[OH^-] = 1.00 \times 10^{-3}$ M) to be 1.5 M^{-1} s^{-1}. In a separate experiment, H_2 and H_5 in [CpRu(η-thiophene)]BF_4 were found to undergo no measurable exchange in d_4-methanol in the absence of base after approximately 4 minutes. However, after 50 minutes, approximately 60% exchange had occurred. Complete exchange occurred in less than 2 h.

Rates of $H_{3,4}$ exchange in **1-4** were slower than for $H_{2,5}$ and were followed readily by ^1H NMR. Values for k_{obsd} are shown in Table I. Examination of rates over at least a 5-fold KOH concentration range showed a linear dependence of the rate on KOH concentration (eqn. 4). Values of the second order rate constant, k, are shown in Table II.

Rates of deuterium incorporation into the methyl substituents in **2**, **3**, and **4** were also monitored. Only small amounts of CH_3 exchange, (approximately 10%) were seen in the ^1H NMR spectra of **2** in the presence of 0.050 M KOH during a 4 h period and **3** in the presence of 0.050 M KOH during 6 h. In a study of complex **2**, over 15 h with 0.040 M KOH, splitting of the methyl singlet due to coupling of the methyl hydrogens with incorporated deuterium was observed. Still, only 30% of the methyl hydrogens were exchanged. The rate constant, k for methyl exchange (Table II) was estimated from a first-order plot of data from this run. For complex **4**, with the 2,5-DMT ligand, less than 10% of the methyl hydrogens were exchanged in the presence of 0.2 M KOH over a period of 4 hours. The estimated rate constant k_{obsd} for this run is in Table II.

DISCUSSION

Mechanism of Deuterium Exchange in CpRu(thiophene)$^+$ Complexes. The rate law (eqn. 4) with a first-order dependence on the OH^- concentration suggests that all of the exchange reactions occur by a mechanism in which OH^- removes H^+ from the thiophene in the slow step; this is followed by rapid deuterium (D^+) transfer to the intermediate from the solvent to give the deuterated product (e.g., eqn. 5). The rates of exchange of the different types of



(5)

hydrogen in complexes **1-4** decrease in the order: $H_{2,5} > > H_{3,4} > CH_3$ Figure 2.1. It is not entirely clear why $H_{2,5}$ are so easily deprotonated. Perhaps the lone pair resulting from deprotonation is stabilized by the vacant d orbitals of the adjacent sulfur, as has been suggested for sulfur-stablized carbanions.[12] It should also be noted that the α hydrogens in free thiophene are relatively more

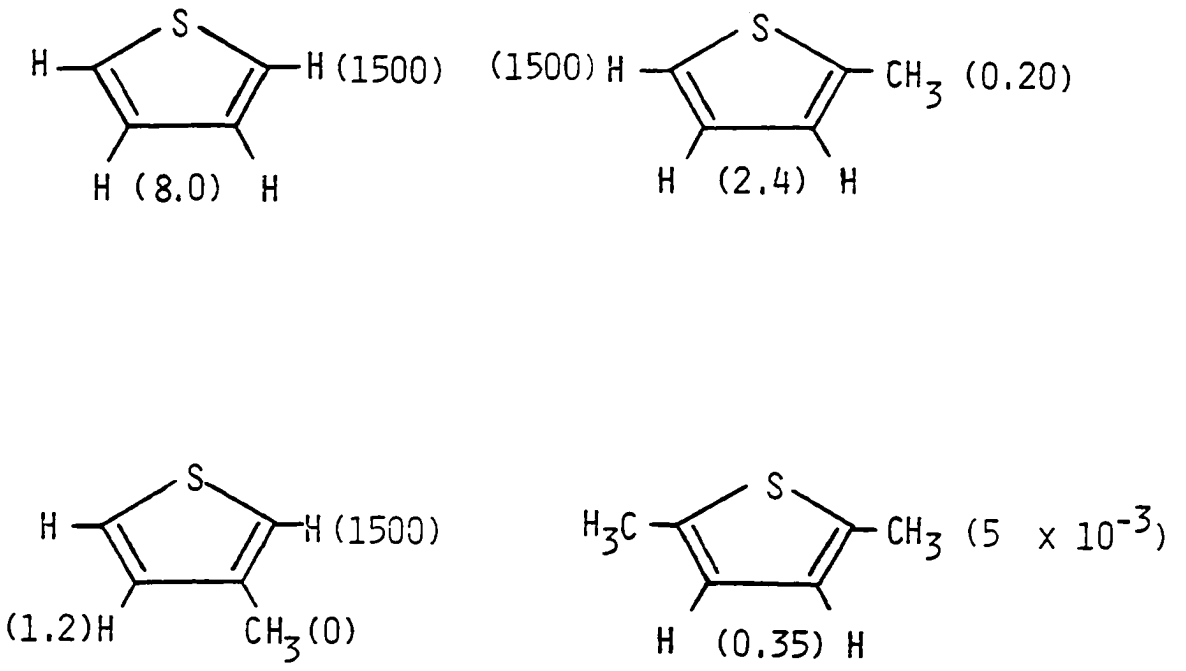
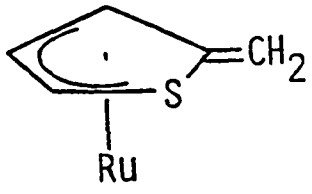


Figure 2.1. Rate Constants $10^3k(M^{-1}s^{-1})$ for Deuterium Exchange in 1-4 Complexes

acidic than those in the β positions.[13] Thus, the 2,5 hydrogens can be deprotonated with lithium alkyls much more readily than the 3,4.[14] Metallation of the 2,5 positions in $Cr(CO)_3$(thiophene)[15] with lithium alkyls also occurs. The observed rates of exchange for H_3 and H_4 in **1**, **2**, and **4** and H_4 in **3** decrease in the order **1** > **2** > **3** > **4**. Presumably, the increased electron density donated by substituent methyl groups in **2**, **3**, and **4** reduce the rate of proton abstraction by OH^- (eqn. 3) by making the exchanging protons less acidic. For **2**, where it might be expected that rates of exchange for H_3 and H_4 might differ, exchange of each of the protons was followed separately. First-order plots of H_3 differed from those for H_4 by no more than 5%. It is interesting that β-hydrogen exchange for **3** is a factor of 2 slower than **2**, presumably due to some electronic effect of the methyl at position 3.

The exchange of protons in the CH_3 groups is very slow. Deprotonation of the CH_3 groups in **2**, **3**, and **4** would give exocylic methylene complexes e.g.,



Related complexes have been obtained by deprotonation of CH_3 groups in π methylbenzene complexes of Ru, Fe, and Mn.[16] In the present

systems, it appears that such exocylic methylene complexes are not sufficiently stable to promote rapid deuterium exchange into the CH_3 groups.

Deuterium Isotope Effect in the Exchange of [CpRu(η-thiophene)] PF_6. For an exchange mechanism (eqn. 5) involving rate-determining C-H deprotonation by OH^-, one would expect the exchange in the deutero analog, [CpRu(η-d_4-thiophene)$^+$, to be 5-7 times slower than in **1**, as is found in other base-catalyzed deprotonation reactions.[17] To determine the isotope effect in this system, the appearance of the η-thiophene proton signals of **1** in a solution of [CpRu(η-d_4-thiophene)$^+$ and 0.05 M KOH in CH_3OH were followed. The signals for $H_{2,5}$ had grown in completely within 10 min of starting the reaction; thus, this exchange was too fast to be studied, as was also the case for **1** with CD_3OD.

No detectable exchange of $H_{3,4}$ in [CpRu(η-thiophene)$^+$ was observed by ^1H NMR after 40 min. After 4 h weak $H_{3,4}$ signals of **1** were apparent, but decomposition of the complex was indicated by darkening of the reaction mixture and by the appearance of free thiophene in the spectrum. Because of this decomposition, and the possibility that OH^- was consumed in the decomposition reaction, the rate of exchange was estimated after 40 min when no decomposition was evident. At this time, no more than 15% of **1** could have formed; this gives an upper limit for the second order rate constant k_D of 1.4 x 10^{-3} M^{-1} s^{-1}. This constant together with that (k_H) for the exchange

of 1 gives a k_H/k_D ratio of at least $(8.0 \times 10^{-3}\ M^{-1}\ s^{-1})/(1.4 \times 10^{-3}\ M^{-1}\ s^{-1}) = 5.7$, a deuterium isotope effect which is consistent with the mechanism in eqn. 5 involving rate-determining deprotonation

Relevance to Catalytic Hydrodesulfurization. In deuterium exchange studies of thiophene over HDS catalysts (eqn. 1), exchange is seen primarily at the 2 and 5 positions with only small amounts of exchange in positions β to the sulfur.[4] Relatively few deuterium exchange studies have been reported for substituted thiophenes. Smith et al.[4a] investigated exchange of thiophene, 2-MT, 3-MT, and 2,5-DMT over supported molybdenum catalysts at 200°C. They report the amounts of mono (d_1)-, di (d_2)-, tri (d_3)-, and tetra (d_4)-deuterated thiophenes obtained under the same conditions. In all cases, the amounts of non-deuterated thiophenes (d_0) were small. Using their data, we calculated the amounts of deuterium incorporated at each of the three types of positions on the ring, α, β, and CH_3. Two assumptions were made in these calculations. First, the α hydrogens of thiophenes exchange before the β hydrogens. This assumption is supported by several studies. Smith et al. [4a] in their exchange studies of thiophene on supported catalysts, Mo/Al_2O_3 and $Co\text{-}Mo/Al_2O_3$ at 200°C, found by NMR analysis that positions 2 and 5 contained most of the deuterium. For 2-methylthiophene and 3-methylthiophene mainly 5 deutero-2-methylthiophene and 2,5-dideutero-3-methylthiophene were formed.[4a] Cowley[4d] also found by deuterium NMR that exchange occurs primarily at the α positions. Kieran and Kemball analyzed thiophene exchanged over MoS_2 at 240° by ^1H NMR.[18] Greater than 95% of the

exchanged hydrogens were found to be α hydrogens. Second, it is assumed that β hydrogens exchange prior to those in the methyl groups.[4a] Smith et al.[4a] as well as Cowley[4d] see only minor amounts of deuterium in α methyl groups, and none in β methyls, e.g., in 3-methylthiophene.

Using these assumptions, we calculate the percent hydrogen at each position which has been substituted by deuterium studies, over a molybdenum/Al_2O_3 catalyst at 200°C[4a] Figure 2.2. For thiophene, 96% of all the hydrogen at $H_{2,5}$ was substituted with deuterium, while only 5.2% of the β hydrogens exchanged. For 2-methylthiophene, most of the α hydrogen at C_5 exchanged, but a very small fraction of the methyl hydrogens did. The results in Figure 2.2 indicate the relative amounts of exchange over the Mo/Al_2O_3 catalyst as $H_{2,5} > H_{3,4} > CH_3$. For the model complexes 1-4, the rates of exchange (Figure 2.1) for the three types of hydrogens decrease in the same order: $H_{2,5} > H_{3,4} > CH_3$. Although $H_{2,5}$ exchange more rapidly than $H_{3,4}$ both in the complexes 1-4 and on the catalyst, the differences between these rates are much larger in the complexes. It is not clear why this is true, and to what extent this difference is affected by the metal and its other ligands.

If one compares just the monomethylthiophenes, exchange of H_4 in 3-MT is slower (or less extensive) than $H_{3,4}$ in 2-MT in the complexes, (Figure 2.1) and also over the catalyst, Figure 2.2. Although it is not clear why a 3-methyl group slows exchange at H_4 more than a 2-methyl group, the effect is the same in the complexes and on the catalyst.

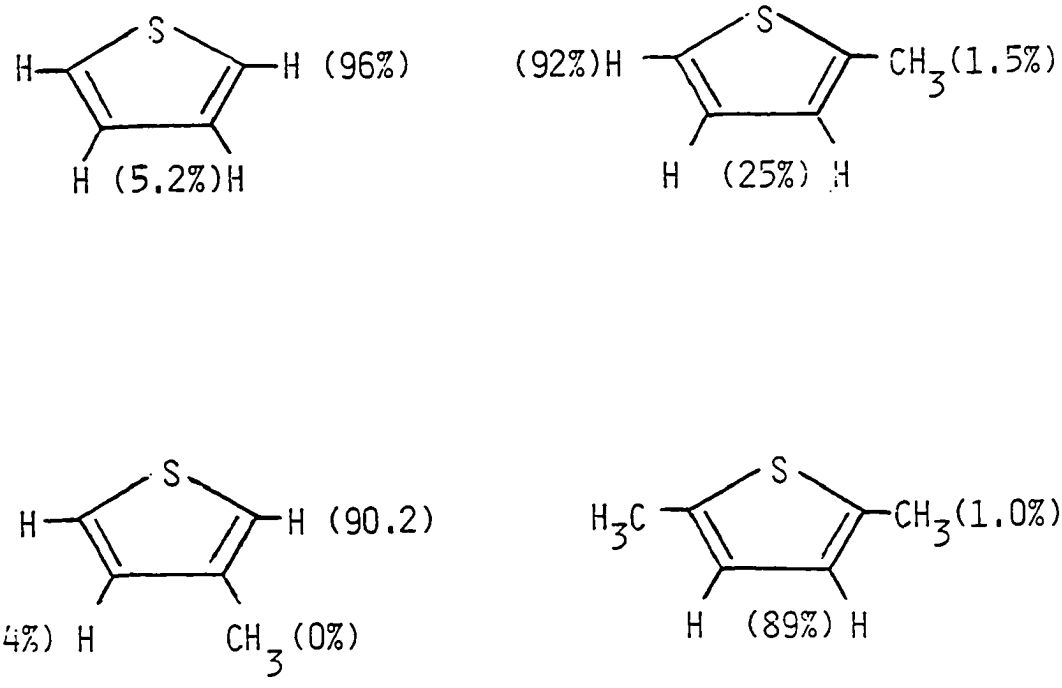


Figure 2.2. Percent Deuteration in Thiophene 2-methylthiophene, 3-methylthiophene, and 2,5-dimethylthiophene over Mo/Al_2O_3 at 200°C.[4a]

The same trend in rates of deuterium exchange in complexes **1-4** and on HDS catalysts suggests that thiophene is π bonded to a metal site (e.g., Mo) on the catalyst. A basic site, e.g. S^{2-} or O^{2-} (on the alumina support) could abstract a proton; deuteration by an acidic SD^- or OD^- would give the deuterated product. Both SH^- and S^{2-} groups are present on HDS catalysts.[19] In earlier studies, Spies and Angelici[7c] showed that Al_2O_3 deuterated with D_2O, was capable of exchanging with $H_{2,5}$ in **1**. The exchange was proposed to be catalyzed by basic oxygen groups on the Al_2O_3 surface.

Relative amounts of $H_{3,4}$ exchange in the differently substituted thiophenes over heterogeneous catalysts are different from the relative rates of exchange in the model complexes **1-4**. That is, over HDS catalysts the amounts of $H_{3,4}$ exchange (Figure 2.2) decrease in the order: 2,5-DMT > 2-MT > 3-MT > thiophene[4a,5a]; whereas the rates of $H_{3,4}$ exchange in the complexes decrease as: thiophene > 2-MT > 3-MT > 2,5-DMT. This difference in trends may be explained by considering that over the catalyst the extent of exchange is dependent not only on the rate of exchange of the absorbed thiophene but also on the amount of the thiophene that is adsorbed. In fact, competitive adsorption studies by Zdrazil[5,20] on $CoMo/Al_2O_3$ give relative adsorption capacities in the order: 2,5-DMT (2.5) > 3-MT (~ 1.7) $\geq$ 2-MT (1.6) > thiophene (1.0).[21] Thus, the thiophenes with the most methyl groups adsorb to the greatest extent and should therefore have the greatest opportunity to undergo deuterium exchange. And this is the order of exchange that is observed. Thus, the extent of

adsorption is more important than the opposing trend which would suggest that the more methyl groups in a π-adsorbed thiophene the slower its deuterium exchange.

While the model studies presented herein do not prove that deuterium exchange of thiophenes on HDS catalysts proceeds via a π-adsorbed thiophene intermediate, they do provide for the first time experimental results that account for the observed amounts of exchange in the various positions of thiophenes over HDS catalysts. The mechanism of exchange in the model system also suggests that basic sites on the catalyst surface are important in promoting the exchanges; presumably more basic supports than Al_2O_3 would increase the rates of exchange, a possibility that could be examined experimentally.

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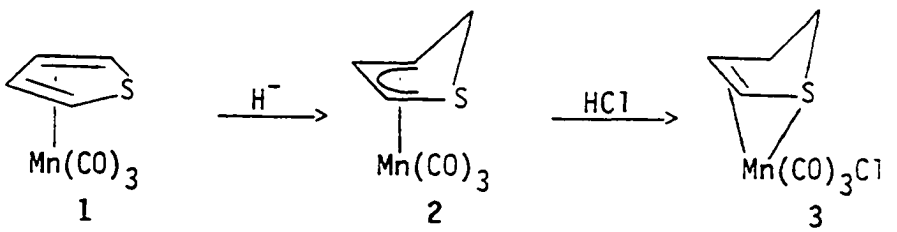
20. Adsorption studies were accomplished by pulsing the thiophenes, and mixtures of thiophenes through a column packed with Co-Mo/Al_2O_3 catalyst at 350° under He. Relative adsorptivities were obtained from retention times.

21. It should be noted that the thiophene adsorption sites in these studies need not be the same sites where deuterium exchange occurs. Thus, the adsorption results may not be related to the deuterium exchange process.

SECTION III. A MECHANISM FOR THE HYDRODESULFURIZATION OF THIOPHENE BASED ON CATALYTIC REACTOR AND MODEL COMPLEX STUDIES OF 2,3- AND 2,5-DIHYDROTHIOPHENE

COMMUNICATION

Catalytic hydrodesulfurization (HDS), the process by which sulfur is removed from crude oils by treatment with H_2 over a Mo-Co/Al_2O_3 catalyst, is one of the largest-scale chemical processes practiced in the world.[1] Because of its commercial importance, many studies have been directed toward understanding the mechanism of the HDS of thiophene, a model compound typical of the organosulfur compounds which are most more difficult to desulfurize organosulfur compounds in petroleum.[2] Despite this effort, most features of the mechanism, including the mode of thiophene binding to the catalyst surface and the nature of the first steps in the process, are still not established. As a model for thiophene π-bonded on the catalyst surface, $[Mn(CO)_3(\eta\text{-thiophene})]SO_3CF_3$, 1, was reacted[3] with the metal hydrides, $PPN[HFe(CO)_4]$ and $PPN[HW(CO)_5]$, as models for hydrides proposed to exist on HDS catalysts;[4] this reaction gave the neutral adduct $Mn(CO_3(\eta\text{-thiophene}\cdot H)$, 2, eqn. 1. Adduct 2 reacted with strong acids such as HCl, a model for acidic surface SH sites,[5] to give complex 3 with a 2,3-dihydrothiophene (2,3-DHT) ligand. Based on

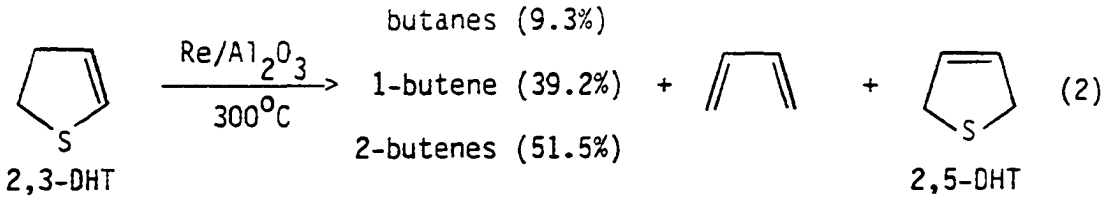


(1)

these model studies, 2,3-DHT was proposed[3] as a possible intermediate in the HDS of thiophene. Others[2b,4b,6] have also suggested that partial or complete hydrogenation of the thiophene ring occurs before the sulfur is removed from the ring. If it is assumed that 2,3-DHT is an intermediate in the HDS of thiophene, then one asks how 2,3-DHT is converted on the catalyst to the observed H_2S and C_4 (butane, 1-butene, and 2-butenes) products. Reactor studies described herein demonstrate that 2,3-DHT is indeed converted to the thiophene HDS products; moreover, our results allow, for the first time, the formulation of a detailed mechanism for the overall HDS of thiophene.

If 2,3-DHT is an intermediate in thiophene HDS, it must undergo desulfurization more rapidly than thiophene because 2,3-DHT has never been reported as a product of thiophene HDS. Indeed, in reactor studies at 400°C over a 5% Re/Al_2O_3 catalyst,[7] only 23.2% of the thiophene reacts, whereas all of the 2,3-DHT[8] is converted to products under the same conditions[9]. It is especially notable that the C_4 product distributions[10] are the same for both thiophene and 2,3-DHT which is consistent with at least part of the thiophene being desulfurized via a 2,3-DHT intermediate.

When the reactor runs were done at 300°C, the C_4 product distributions were not the same for thiophene and 2,3-DHT.[11] The products of the 2,3-DHT reaction contained butadiene (10.9%) and 2,5-DHT (11.5%), in addition to the usual C_4's (8.3%), thiophene (14.4%) and tetrahydrothiophene (54.9%), eqn. 2. The formation of both 2,5-DHT, and butadiene suggests that desulfurization might occur by



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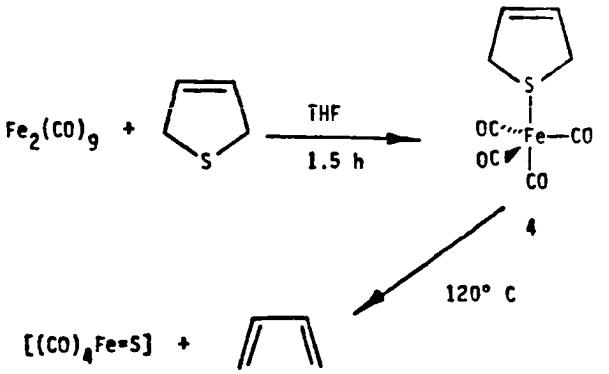
isomerization of 2,3-DHT to 2,5-DHT, and in a further step, by elimination of S from 2,5-DHT, to give butadiene. This proposal is supported by HDS reactor studies of 2,5-DHT[12] at 300°C, where more than 60% of the desulfurized product was butadiene.[13] Moreover, when this reaction was carried out in the presence of D_2 rather than H_2, 65% of the butadiene product contained no deuterium, suggesting that 2,5-DHT eliminates butadiene directly, rather than first isomerizing to 2,3-DHT.[14] Since the elimination of butadiene is likely to occur when the 2,5-DHT is coordinated via the sulfur to a metal site on the catalyst, [15] we explored the possibility that this reaction would take place in a simple transition metal complex.

The room temperature reaction of $Fe_2(CO)_9$ with 2,5-DHT, eqn. 3 in dry tetrahydrofuran (THF) gives $(CO)_4Fe(2,5\text{-DHT})$, **4**, which was isolated as an unstable red-brown oil[16]. A small amount of 4 was heated in an evacuated nmr tube at 120°C for 10 min, giving a



(3)

black solid. The tube was cooled in an ice bath, $CDCl_3$ was added by syringe, and the ^1H nmr spectrum taken. Resonances for only butadiene (~30%) and free 2,5-DHT (~70%) were observed. The formation of butadiene was confirmed by G.C.-M.S. analysis of the gaseous products of the decomposition. The initial inorganic product of the reaction would presumably be $Fe(CO)_4(=S)$; however, since only an insoluble black solid (presumably FeS) is observed, the putative $Fe(CO)_4(=S)$ intermediate apparently decomposes rapidly at 120°C with loss of CO. Regardless of the inorganic product, reaction 3 clearly demonstrates that metal coordination to 2,5-DHT promotes the elimination of butadiene, as suggested by the reactor studies.

The reaction of 2,3-DHT with $Fe_2(CO)_9$ did not yield a characterizable $Fe(CO)_4$(2,3-DHT), but when run in d_6-acetone in an NMR tube, small amounts of 2,5-DHT were observed, which demonstrates that the metal promotes the isomerization of 2,3-DHT to 2,5-DHT,[17] a process that was also observed in the reactor studies.

The combined results of the reactor studies, the model reactions of $Fe_2(CO)_9$ with 2,3- and 2,5-DHT (eqn. 3) and the reactions (eqn. 1) of $[Mn(CO)_3(\eta\text{-thiophene})]SO_3CF_3$ suggest the overall mechanism for the HDS of thiophene presented in Figure 2.1 This involves initial π-coordination of the thiophene to a metal site, surface hydride transfer to the 2-position of thiophene, followed by H^+ addition from an SH group to the 3-position. The resulting 2,3-DHT may be coordinated via the sulfur and olefinic bond as shown in Figure 2.1 or only via the sulfur.[15] After isomerization of 2,3-DHT to 2,5-DHT, butadiene is eliminated leaving a surface sulfide which could be removed as H_2S upon reaction with hydrogen. The butadiene would be hydrogenated to the observed mixture of C_4 products. Although our studies do not prove that this is a mechanism for thiophene HDS, it is the first complete mechanism which is based on demonstrated reactions of thiophene and dihydrothiophenes in model transition metal complexes and on HDS catalysts.

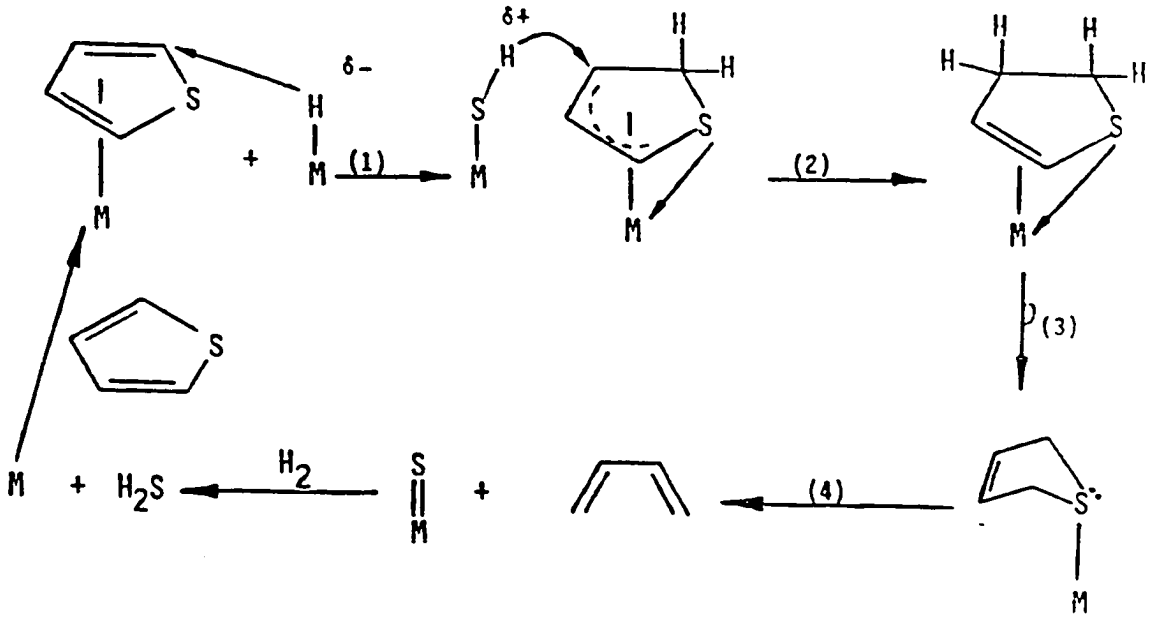


Figure 2.1. Proposed mechanism for thiophene desulfurization

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7. Reactor studies were done using a continuous flow catalytic microreactor packed with 5 wt % Re/Al_2O_3, with H_2 as the carrier gas. The catalyst was prepared by aqueous impregnation of Re_2O_7 into a calcined Al_2O_3 support (175 m^2/g), followed by vacuum

drying and slow reduction in H_2 at 400°C. The reduced catalyst, (0.12 g) was loaded into a 1/16" ID stainless steel reactor and was sulfided for 4 hr in flowing H_2/thiophene prior to experiments. Reaction products were identified using a dedicated G.C. and ^1H nmr.

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9. The thiophene products are only desulfurized C_4 hydrocarbons, whereas 2,3-DHT gives 80.8% desulfurized hydrocarbons and 19.2% thiophene.
10. 19% butane, 18% 1-butene, 63% cis- and trans-2-butene for thiophene and 2,3-DHT.
11. 19.1% butane, 18.1% 1-butene, and 61.5% 2-butenes for thiophene and 9.3% butane, 39.2% 1-butene, and 51.5% 2-butenes for 2,3-DHT.
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13. The total C_4 product distribution was 63.5% butadiene, 1.3% butane, 11.8% 1-butene, and 23.4% 2-butene.
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15. It is possible that a relatively small amount of 2,3-DHT is converted to butadiene by a mechanism not involving isomerization to 2,5-DHT.

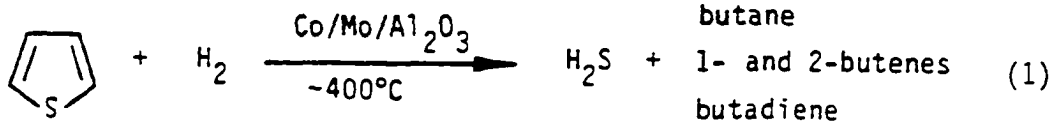
16. ^{1}H NMR (acetone): δ 5.99 (2H, s, $H_{3,4}$), 4.01 (4H, s, $H_{2,5}$). ^{13}C NMR (acetone): δ 127.64 ($C_{3,4}$), 52.87 ($C_{2,5}$). EIMS: m/e 254 (parent ion = M^+), 226 (M^+-CO), 198 (M^+-2CO), 170 (M^+-3CO), 86 (DHT^+) base peak. IR (pentane): 2045 w, 1965 m, 1939 s. The compound was too unstable for elemental analysis.

17. Iron carbonyl fragments are known to catalyze the isomerization of other olefins. (a) Wrighton, M. S.; Ginley, D. S.; Schroeder, M. A.; Morse, D. L. Pure Appl. Chem. **1975**, 41, 671. (b) Wrighton, M. S. Chem. Rev. **1974**, 74, 401.

SECTION IV. HYDRODESULFURIZATION AND DEUTERODESULFURIZATION OF 2,3- AND 2,5-DIHYDROTHIOPHENES; AN INVESTIGATION OF THE MECHANISM OF THIOPHENE HYDRODESULFURIZATION

INTRODUCTION

Catalytic hydrodesulfurization (HDS) is extensively used in industry in the production of fuels and petrochemical feedstocks.[1] While much recent research has centered on the characterization of industrial catalytic materials,[2] relatively little is known about the mechanism of HDS. This paper is concerned specifically with the mechanism of HDS of thiophene (Th) which is representative of the less reactive organosulfur compounds in petroleum.



(1)

Hydrogenation of the thiophene ring to 2,3-dihydrothiophene (2,3-DHT) has been proposed as the initial step in the desulfurization process. This disrupts the aromatic stabilization of the ring, presumably a major barrier to the overall HDS process.[1,3] Subsequent C-S bond cleavage eventually gives desulfurized the products, butadiene, 1- and 2-butenes, and butane. Despite the proposed intermediacy of 2,3-DHT, only a single reactor study of 2,3-DHT has been reported.[4] In early work by Desikan and Amberg, the HDS reactivity of 2,3-DHT over a Co-Mo catalyst was compared to that of thiophene and tetrahydrothiophene (THT) at 270-370°C. They found that 2,3-DHT desulfurized at a rate intermediate between that of Th and

THT; thiophene was observed as a product but not THT. No 2,3-DHT was reported as a product of either the Th or THT reaction over the catalyst. A mechanism for 2,3-DHT HDS was not proposed.

In this work, we examined the reactivity of the partially hydrogenated thiophenes, 2,3-DHT and 2,5-DHT, over $Mo/\gamma\text{-}Al_2O_3$ and $Re/\gamma\text{-}Al_2O_3$ HDS catalysts. In particular, we wished to address the questions: (1) Are either or both of the dihydrothiophenes intermediates in the interconversion of thiophene and tetrahydrothiophene over HDS catalysts? (2) Do hydrogenated intermediates provide a route to thiophene desulfurization? (3) What is the pathway for desulfurization of these dihydrothiophenes?

EXPERIMENTAL

General Procedures. Thiophene (Th) and tetrahydrothiophene (THT) were obtained from Alfa products, and were used without further purification. Gas chromatographic analysis of these showed total impurities to be less than 0.3%. ^1H NMR spectra were taken on a Nicolet NT-300 spectrometer using deuterated solvents as internal locks. G.C.M.S. spectra were obtained with a Finnigan 4000 mass spectrometer.

Preparation and Storage of 2,3- and 2,5-Dihydrothiophene (DHT). The 2,3- and 2,5-dihydrothiophenes were prepared as described previously.[5,6] To minimize decomposition of the relatively unstable 2,3-DHT, fresh samples were prepared before each reactor run, and stored under N_2 in a liquid N_2 bath prior to use. The 2,5-DHT is much less susceptible to thermal decomposition and could be prepared in advance and stored at -20 °C under N_2 for 2 weeks without decomposition. ^1H NMR was used to establish purities of 97% or greater for both the dihydrothiophenes.

Catalyst Preparation. The 5% $Re/\gamma\text{-}Al_2O_3$ catalyst was prepared by dry impregnation pore volume filling of a precalcined $\gamma\text{-}Al_2O_3$ support (Armak, ~175 m^2/g). The $\gamma\text{-}Al_2O_3$ support was stirred with an aqueous solution of Re_2O_7 to give a 5 wt % loading of $Re/\gamma\text{-}Al_2O_3$ (~ 1.1ml Re_2O_7 solution for 1 g Al_2O_3). The resultant paste was dried for 12 h under vacuum at room temperature. Calcination was performed at 400 °C for 4 h; then, the catalyst was reduced in flowing H_2 while heating slowly (2°/min) to 400 °C. The catalyst was reduced for 4 h

at 400 °C and then allowed to cool to room temperature under H_2. The reduced catalyst was pressed into 13 mm pellets at 15000 psi, then crushed and sieved to produce uniform 50/100 mesh catalyst particles for use in the microreactor.

The 5% Mo/γ-Al_2O_3 catalyst was prepared by a method similar to that described for the Re catalyst, using aqueous solutions of ammonium heptamolybdate [$(NH_4)_6$ Mo_7O_{24} • 4 H_2O] instead. The paste from dry impregnation of the calcined alumina support was dried under vacuum at 110 °C. The catalyst was reduced at 400°C, as with the Re catalyst, and then crushed and sieved to 50/100 mesh particles to be used in the reactor.

Sulfiding of both the 5% Re and Mo/γ-AL_2O_3 catalysts was performed in situ in a 1.5 mol % stream of thiophene in H_2 for 4 h at 400 °C.

Activity Measurements. The activity measurements were performed in a 1/16 inch diameter stainless-steel reactor operated in a continuous flow mode. Thiophene desulfurization activity of the reactor with a charge of γ-Al_2O_3 at 400 °C was found to be negligible, about 0.06% conversion. The products were separated and analyzed by an Amtek 310 gas chromatograph equipped with an FID detector which could be switched between 2 columns. A 12 inch Porapak Q column (120 °C, 50 ml/min He carrier gas) was used for the determination of overall conversions to C_4 hydrocarbons and for the analysis of thiophene, the dihydrothiophenes and tetrahydrothiophene. Untegrated areas for sulfur containing hydrocarbons multiplied by 0.85 to correct

for FID detector response. An 18 ft 0.19% picric acid/carbopak column (70 °C, 60 ml/min He) separated the C_4 hydrocarbons for analysis. Complete separation of 2,5-DHT and tetrahydrothiophene could not be accomplished using the Porapak Q column. Analysis for these compounds was done with ^1H NMR. Samples of nondesulfurized products, i.e., thiophene, 2,3- and 2,5-DHT, and tetrahydrothiophene were collected at -78 °C in a removable quartz tube attached to the reactor vent line. The trap, which could be removed under H_2 flow, was kept at -78 °C until samples were analyzed by ^1H NMR.

Hydrodesulfurization activities of both catalysts for all feeds were measured under 1 atm H_2 pressure. For a typical run, 0.122 g of catalyst charge was packed between pyrex wool plugs. Reactants were introduced into the reactor by continuous injection of the feed into a 10 inch length of 1 inch diameter tubing which allowed mixing of the reactant with the H_2 carrier gas. Catalyst activity measurements, (conversion to C_4 hydrocarbons) and C_4 product distributions were taken, and the feed switched to the 2,3-dihydrothiophene or tetrahydrothiophene. A period of 1.5 to 2 h was allowed to flush the feed system of thiophene before taking conversion and product distribution data for the new feed. During the run, no substantial (< 5%) deactivation of the catalyst, as tested by conversion of thiophene to C_4 hydrocarbons, was observed.

Deuterodesulfurization (DDS) Studies of 2,3- and 2,5-DHT. Deuterodesulfurization studies were done with the same reactor system as the HDS runs. For the DDS studies, the catalyst was brought on

stream in flowing H_2/thiophene. After about 4 h, when thiophene desulfurization levels were constant, the feed was switched to either 2,3- or 2,5-DHT. The system was allowed to stabilize for 2 h, and gas samples of unexchanged 2,3- or 2,5-DHT HDS products for mass spectrometric analysis were collected in a 500 ml gas sampling bulb attached to the line after the reactor. These samples were used to establish the parameters for G.C.M.S. analysis of the deuterated samples. Samples of unexchanged 2,3- or 2,5-DHT HDS products for ^1H NMR analysis were collected as indicated earlier. The carrier gas was then switched to D_2, the reactor system equilibrated under D_2 for 2 h, and samples for G.C.M.S. and ^1H NMR were taken as before.

Mass spectra were collected on a Finnigan 4000 spectrometer using low electron energy of 12 ev to reduce fragmentation of the molecular ion peak to less than 5%. Using the MS data from undeuterated HDS products, corrections for naturally occurring deuterium, and fragmentation of the parent ion in the mass spectrometer were applied to the MS data obtained for deuterated samples.

RESULTS

Tables I and II show the conversion levels and product distributions for the HDS reactions of Th, 2,3-DHT, 2,5-DHT and THT HDS at 400 and 300 °C over the 5% $Re/\gamma-Al_2O_3$ catalyst. At reaction temperatures of 400 °C, conversions to C_4 hydrocarbons increase in the order Th < THT < 2,5-DHT < 2,3-DHT. Only 23.2% of the thiophene undergoes desulfurization to C_4 hydrocarbons, while 67.7 and 74.2% of the 2,3- and 2,5-DHT are converted to C_4's. Small amounts of thiophene (3.1%) were observed from THT HDS at 400°C as well. No 2,3-DHT or 2,5-DHT were seen as products of either Th or THT HDS. The C_4 product distributions (Table II) for thiophene and 2,3-DHT at 400°C were essentially the same (~19% Butane, ~19% 1-butene and 62% 2-butene). Tetrahydrothiophene produces relatively more of the fully saturated product, butane and less of 2-butene, while 2,5-DHT product streams had approximately half of the butane that are seen for the other feeds (10%), and greater than thermodynamic equilibrium amounts of 2-butenes, (a 1:3.2 ratio of 1-butene:2-butenes rather than the thermodynamic ratio at 400°, 1:2.85).

At 300 °C, desulfurization of all sulfur compounds (Th, THT, 2,3- and 2,5-DHT) was substantially lower. Conversion of both Th and THT drop to ~2%, but despite the drastic lowering of activity, product distributions (Table II) for thiophene HDS remain similar at 300 and 400 °C. Slightly lower amounts of 1-butene were observed for both Th and THT at 300 °C. For thermodynamic equilbrium at 300°, larger

Table I. Product analysis of 5% Re/Al_2O_3 catalyst at 300 and 400°C

Feed	Temp	Product Analysis					
		C_4's (%)	C_{1-3}'s[a] (%)	Th (%)	2,3-DHT (%)	2,5-DHT (%)	THT (%)
Th	400	23.2	1.8	75.0	0	0	0
	300	2.2	0.2	97.6	0	0	0
THT	400	56.3	6.2	3.1	0	0	34.4
	300	1.6	0.7	0.7	0	0	97.0
2,3-DHT	400	74.2	7.5	18.3	0	0	0
	300	11.5	0.9	8.5	39.6	6.9	32.6
2,5-DHT	400	67.7	6.8	25.5	0	0	0
	300	17.6	1.8	19.1	21.8	13.5	26.2

[a]Only 2,3-DHT, no 2,5-DHT was observed for reactions over Mo/Al_2O_3.

Table II. C_4 product distributions for 5% Re/Al_2O_3 catalyst at 300 and 400°C

Feed	Temp (°C)	Conversion (%)	C_4 Product Distribution			
			Butane (%)	1-Butene (%)	2-Butene (%)	Butadiene (%)
Th	400	23.2	19.1	18.1	62.8	0
	300	2.2	22.3	13.2	64.3	0
THT	400	56.3	23.9	18.2	57.9	0
	300	1.6	28.5	13.7	57.8	0
2,3-DHT	400	74.2	17.7	18.9	63.4	0
	300	11.5	4.0	16.9	22.2	56.9
2,5-DHT	400	67.7	10.0	21.4	68.6	0
	300	17.6	1.3	11.8	23.4	63.5

amounts of 1-butenes would expected (a 1-butene:2-butene ratio of 1. 2.46). In contrast to the distributions for Th and THT, products observed for 2,3-DHT HDS at the lower temperature were radically different than those seen at 400 °C. Butadiene is the major desulfurized product, and 2,5-DHT is formed in addition to butenes, Th, and THT. While 1-butene levels are relatively constant at 300 and 400°C, a significant decrease in the 2-butene products (63.3 to 22.2%) is observed. Likewise, for 2,5-DHT, butadiene is the major desulfurized product, and isomerization to 2,3-DHT is also observed.

Conversions to desulfurized products and product distributions for the reactions of Th, THT and 2,3-DHT over the 5% Mo/γ-Al_2O_3 catalyst at 400 and 300 °C are given in Tables III and IV, respectively. At 400°, 2,3-DHT is seen to be the most reactive feed, being entirely converted to desulfurized products, thiophene, and THT. The observation of THT in the product stream was surprising in view of the extremely high reactivity of THT at the higher temperature, where 81.6% conversion to C_4's was observed. For all three feeds, distributions of C_4 products are very similar at 400 °C; 7% butane, 22% 1-butene, and 71% cis and trans 2-butene, corresponding to a nearly thermodynamic distribution of the butenes,[7] (26% 1-butene, 44% trans-2-butene, and 30% cis-2-butene). Thiophene was observed in the product streams of both THT and 2,3-DHT, and THT was formed from 2,3-DHT and Th over the catalyst.

Table III. Product analysis for 5% Mo/Al_2O_3 catalyst at 300 and 400°C

Feed	Temp	Product Analysis				
		C_4's[b]	C_{1-3}'s	Th	DHT[a]	THT
Th	400	24.5	0.8	74.7	0	0
	300	3.8	0.3	95.1	0	0.8
THT	400	81.6	7.1	2.8	0	8.5
	300	2.6	0.9	0	0	96.5
2,3-DHT	400	68.7	8.3	19.6	0	3.4
	300	22.8	4.6	6.5	8.3	57.8

[a]Only 2,3-DHT, no 2,5-DHT was observed for reactions over Mo/Al_2O_3.

[b]Small amounts of cracking products C_1-C_3's were observed for all reactor runs, but were not identified.

Table IV. C_4 product distributions for 5% Mo/Al_2O_3 catalyst at 300 and 400°C

Feed	Temp	Conversion to C_4's	C_4 Product Distribution		
			Butane	1-Butene	2-Butene
Th	400	24.5	7.9	21.8	70.3
	300	3.8	6.5	19.1	74.4
THT	400	81.6	5.5	23.3	71.2
	300	2.6	9.3	42.7	48.0
2,3-DHT	400	68.7	6.3	21.8	71.9
	300	22.8	2.8	47.1	50.1

As with the $Re/\gamma\text{-}Al_2O_3$ catalyst at 300 °C, conversion of Th and THT over $Mo/\gamma Al_2O_3$ at 300° dropped to <5%, while the reactivity of 2,3-DHT remained quite high, with approximately 92% conversion to desulfurized products, Th, and THT. No production of 2,5-DHT from 2,3-DHT was observed over this catalyst, nor was any butadiene detected. While no butadiene was detected under these conditions for desulfurization of 2,3-DHT, twice the amount of 1-butene was produced at 300° than at 400°C.

For three feeds, at both temperatures, reaction over the catalyst produced small amounts of cracking products, C_{1-3}'s. The amount of these lighter hydrocarbons which were formed were quantitated by G. C., however, no attempts was made to identify exactly these compounds.

Deuterodesulfurization studies. These reactor runs were done to examine the pathways for 2,3- and 2,5-DHT interconversion over the 5% $Re/\gamma\text{-}Al_2O_3$ catalyst and the route of butadiene formation from both of these feeds. Conversions to desulfurized products and distributions of C_4 hydrocarbons in the these studies were the same as those seen for HDS runs. Deuterium distributions for 2,5-DHT are shown in Figures 4.1 and 4.2, those for 2,3-DHT DDS in Figure 4.3 and 4.4. The percentage of hydrogen exchanged for deuterium at each of the ring positions in the product thiophene, 2,3-DHT, 2-5-DHT and tetrahydrothiophene for 2,5-DHT DDS and 2,3-DHT DDS are shown in Figures 4.5 and 4.6 respectively.

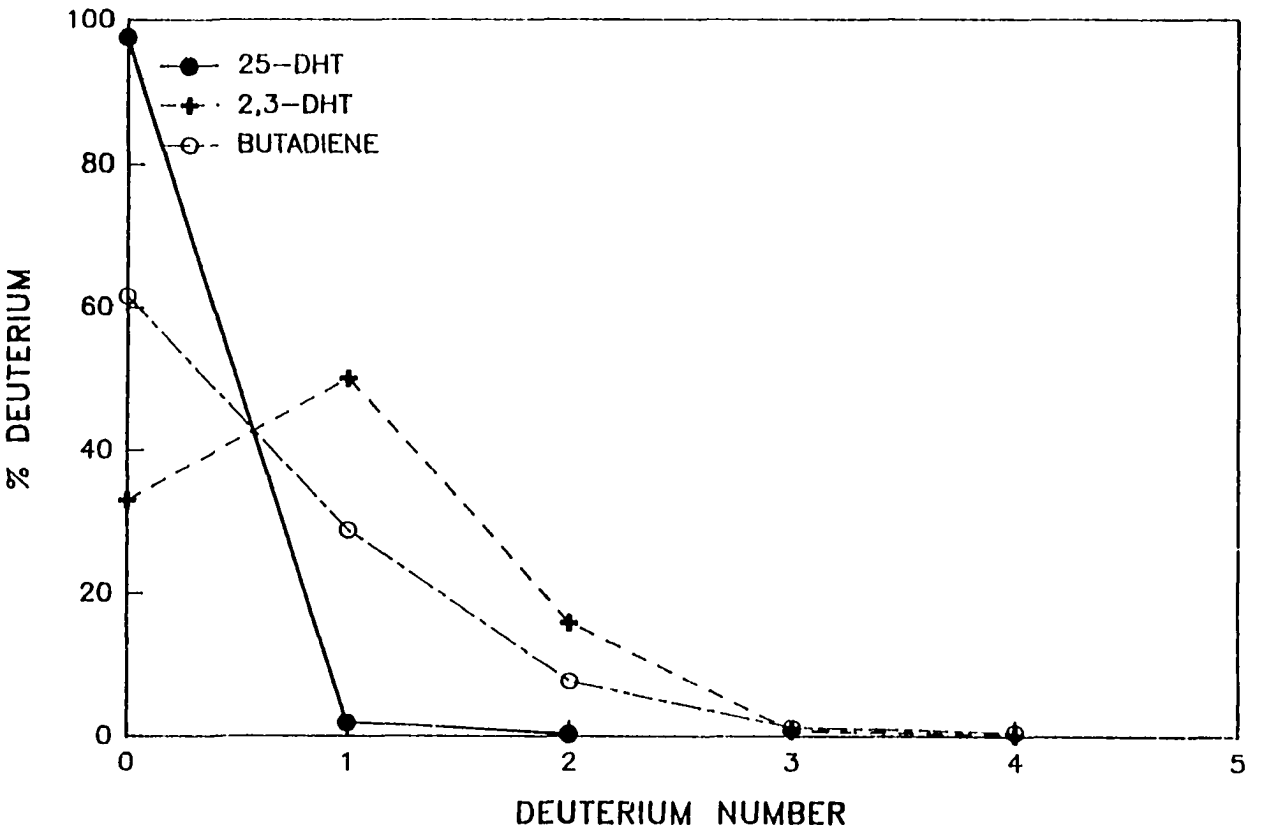


Figure 4.1 Deuterium distributions for 2,5-DHT DDS

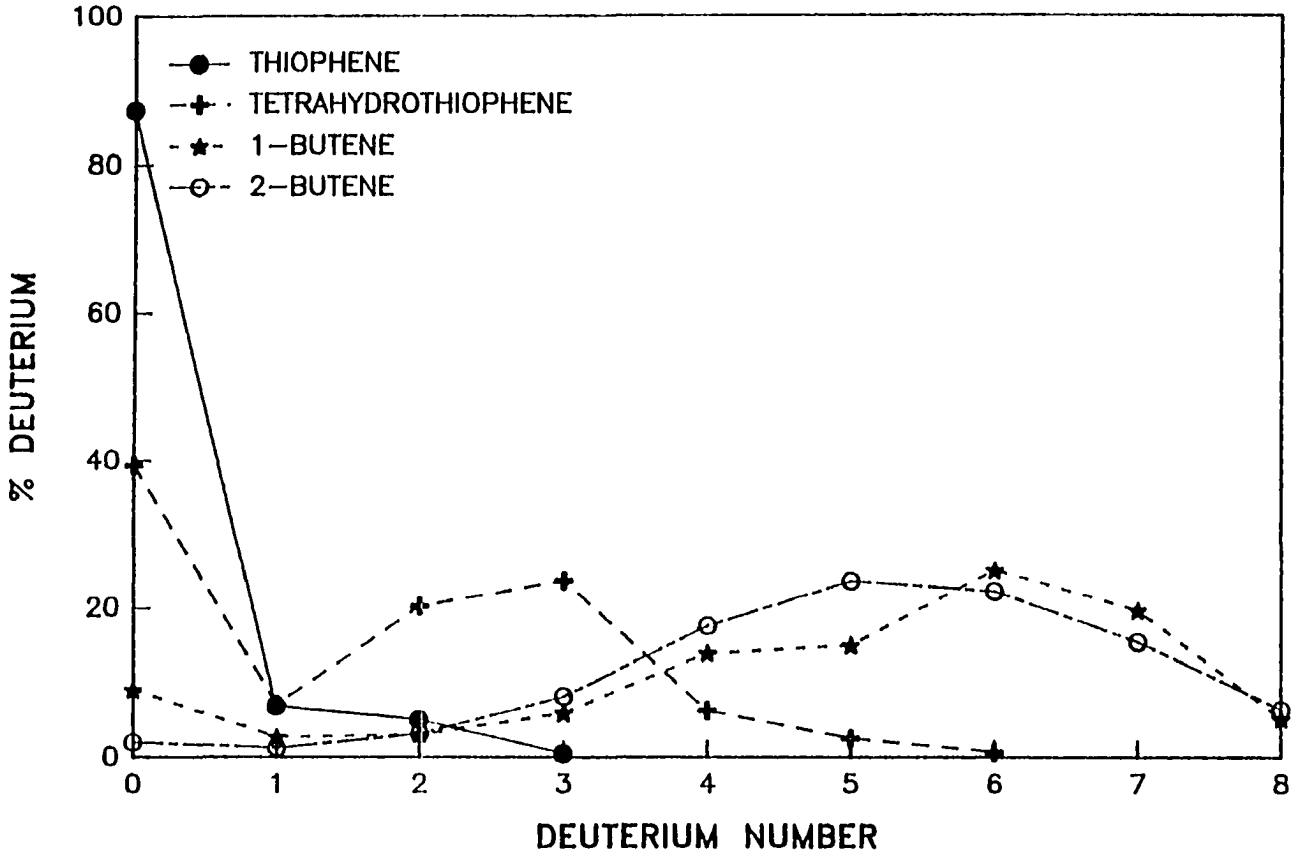


Figure 4.2 Deuterium distributions for 2,5-DHT DDS

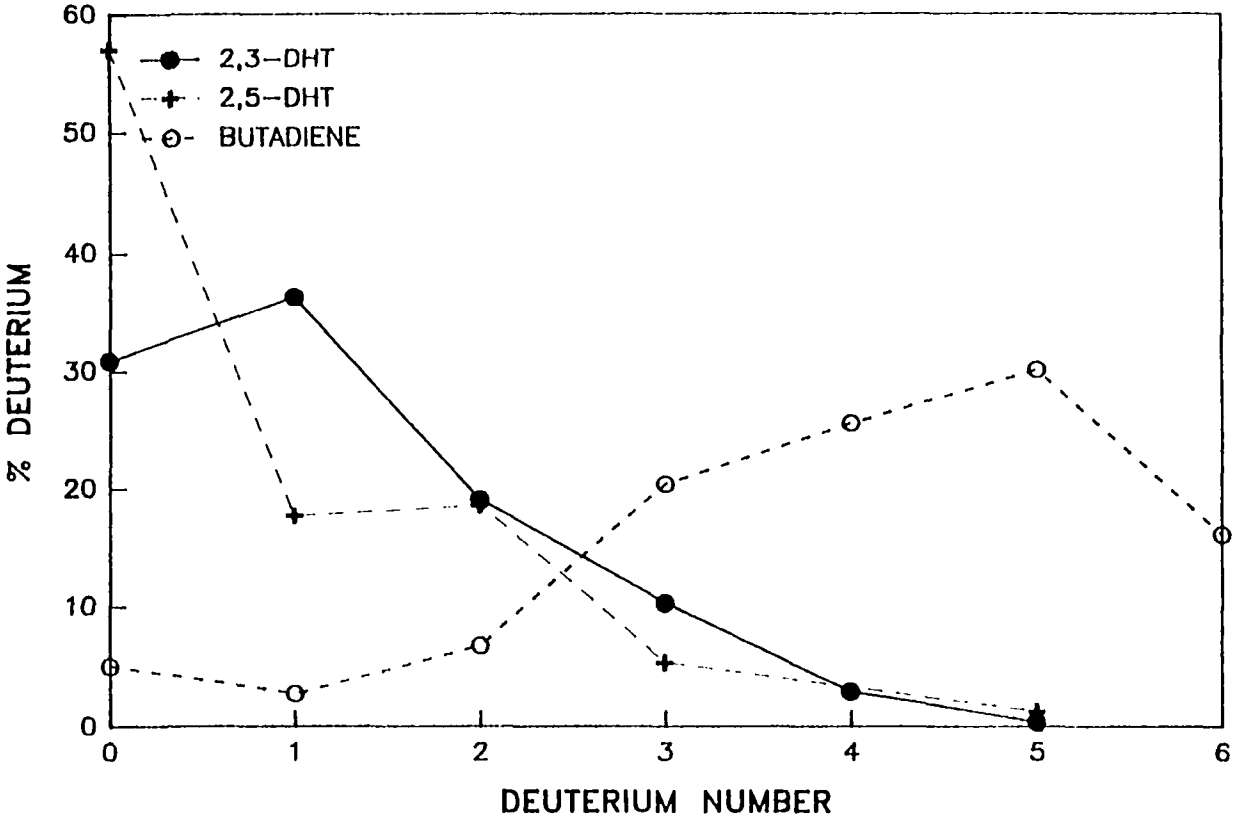


Figure 4.3 Deuterium distribution for 2,3-DHT DDS

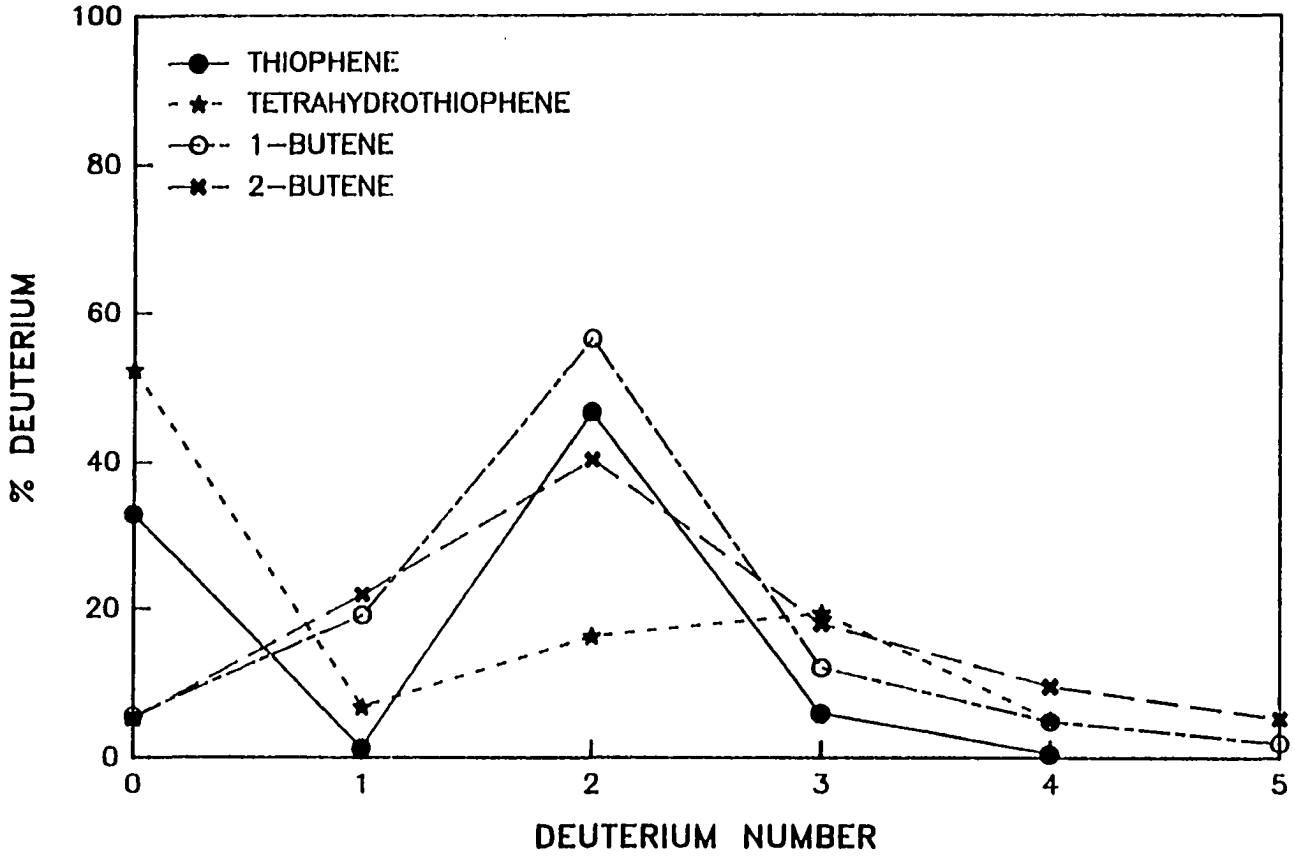


Figure 4.4 Deuterium distributions for 2,3-DHT HDS

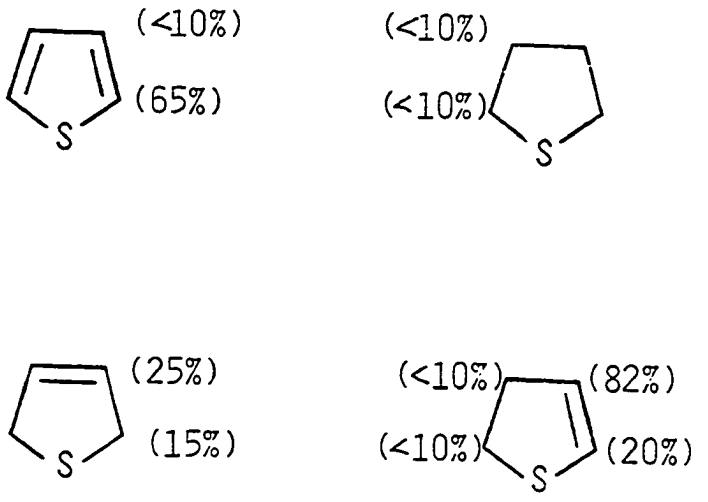


Figure 4.5 Deuterium incorporation into the ring positions of Th, THT 2,3-DHT, and 2,5-DHT from 2,5-DHT DDS

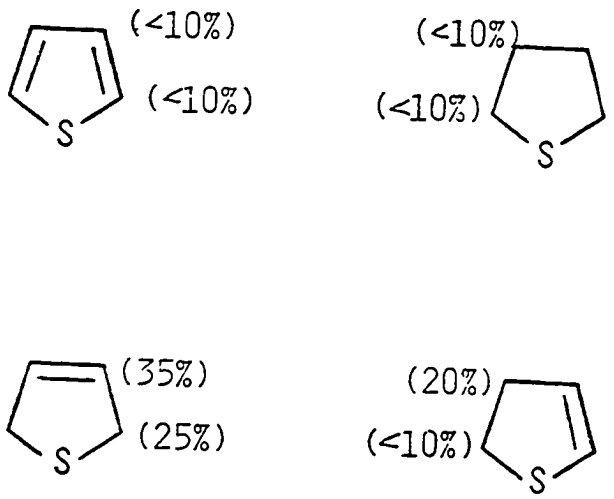


Figure 4.6 Deuterium incorporation into the ring positions of Th, THT 2,3-DHT, and 2,5-DHT from 2,3-DHT DDS

Unreacted 2,5-DHT was not exchanged over the catalyst, with nearly 98% of it being d_0. The majority of the butadiene produced (62%) was also d_0. Only a small percentage of the butadiene (~8%) incorporated more than 1 deuterium. Deuterium content was also low for the 2,3-DHT produced by isomerization of 2,5-DHT; the product being 83% d_0 or d_1. The H_2S was 80% d_0.

In contrast to the low amounts of deuterium generally incorporated into the products of 2,5-DHT HDS, substantial amounts of deuterium were found in several of the 2,3-DHT products. The 2,3-DHT itself d_1 and d_2. However, greater than 85% of the butadiene produced.

DISCUSSION

The interconversion of thiophene and THT over both the $Re/\gamma\text{-}Al_2O_3$ and $Mo/\gamma\text{-}Al_2O_3$ catalysts at 300 and 400°C and the formation of both Th and THT from 2,3- and 2,5-DHT HDS clearly demonstrates the existence of pathways interconverting the different thiophenes (Th, THT and 2,3- and 2,5-DHT) over the catalysts.(Tables I and III). The hydrogenation of Th to THT, and the dehydrogenation of THT to Th, have been suggested to occur via an intermediate surface bound 2,3-DHT.[4] The absence of 2,3-DHT in the product streams of either Th or THT HDS is not in contradiction with this possibility, as 2,3-DHT is highly reactive over both catalysts.

The high desulfurization reactivity of 2,3-DHT makes it possible that in thiophene HDS, at least part of the thiophene desulfurizes via a 2,3-DHT intermediate. Indeed, at 400 °C over both catalysts, the C_4 product distributions (Tables II and IV) for 2,3-DHT and thiophene are essentially identical, as would be expected if 2,3-DHT were an intermediate in Th HDS. In contrast, the HDS products of 2,5-DHT at 400°C (Table II) contained somewhat higher amounts of 1- and 2-butenes and about half the butane that were seen for Th and 2,3-DHT HDS.

The work of several researchers provides strong evidence that butadiene is the initial product in thiophene HDS[7-10], Figure 4.7. Hydrogenation and isomerization of the butadiene give the observed C_4 products, butenes and butane.

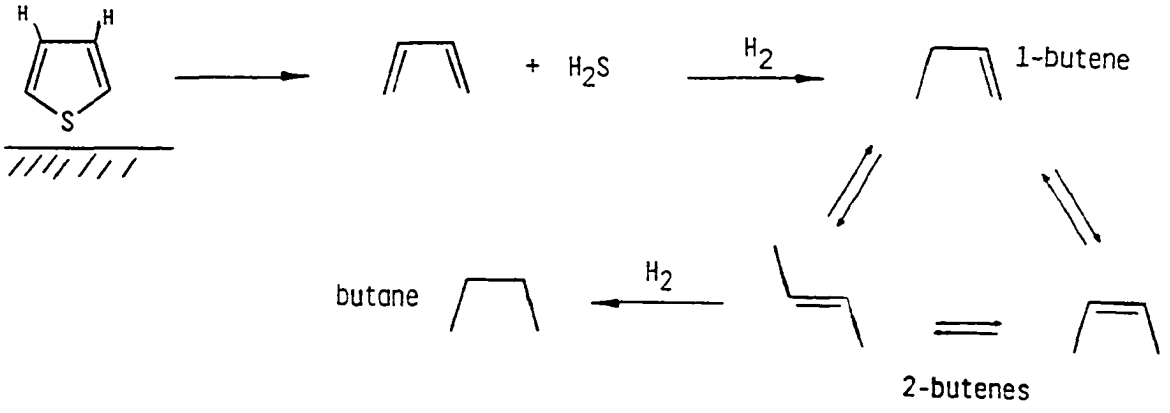
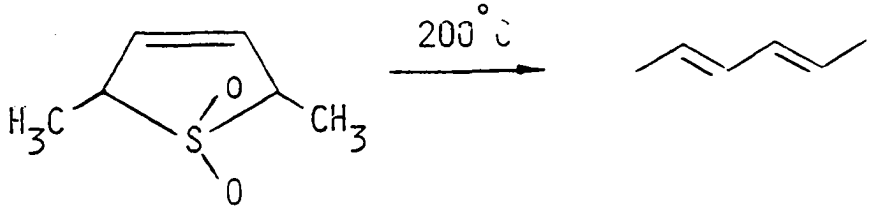


Figure 4.7. Thiophene HDS with butadiene as the initial product

Thus, at 300 °C with the Re/γ-Al_2O_3 catalyst, the fact that butadiene is the major desulfurized product for 2,3-DHT HDS, lends support to the proposal that 2,3-DHT is an intermediate in thiophene HDS. Apparently, at the higher conversions of 2,3-DHT to desulfurized products, (11% versus 2% for thiophene), too much butadiene is produced for the catalyst to hydrogenate and isomerize it to butenes and butane. Thus, large quantities of butadiene and the next product in the sequential pathway, 1-butene, are observed. Thiophene HDS at 300° over Re/γ-Al_2O_3, however, gives a nearly thermodynamic ratio of butenes.[11] Differences in the thiophene and 2,3-DHT C_4 hydrocarbon distributions are not necessarily evidence for different desulfurization pathways. Instead, they may simply reflect the

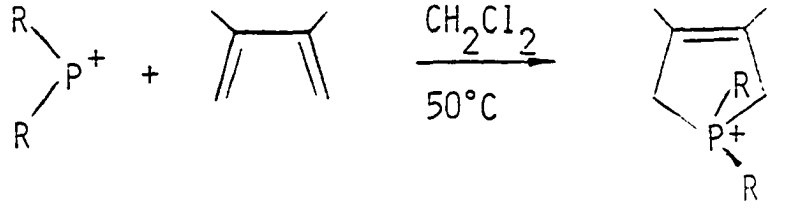
relative rates of desulfurization vs. hydrogenation and isomerization reactions of the butadiene product. Because only 2% of thiophene is desulfurized, the catalyst is able to hydrogenate all of the butadiene formed to butenes or butane. For 2,3-DHT however, where 11.5% undergoes desulfurization, the catalyst is not able to convert all the butadiene, to butenes and butane, and butadiene is observed in the product stream. The absence of THT in the products of Th HDS may also be explained in the same way. At the low conversions of Th, only a small amount of THT is produced, and it readily desulfurizes on the catalyst.

In addition to Th and THT as nondesulfurized products of 2,3-DHT HDS at 300°, the reaction over 5% $Re/\gamma\text{-}Al_2O_3$ also produced 2,5-DHT. This isomerization was not observed earlier by Amberg over their $Co\text{-}Mo/Al_2O_3$ catalyst or by us with $Mo/\gamma\text{-}Al_2O_3$. The formation of both 2,5-DHT and butadiene suggests that desulfurization of 2,3-DHT might occur by isomerization of 2,3-DHT to 2,5-DHT, and in a further step, by elimination of S from 2,5-DHT to give butadiene. A similar type of elimination has been reported for several noncatalytic systems. Vapor phase pyrolysis of 2,5-dihydrothiophene 1,1 dioxides gives the butadiene through loss of SO_2 eqn. 2.[12]



(2)

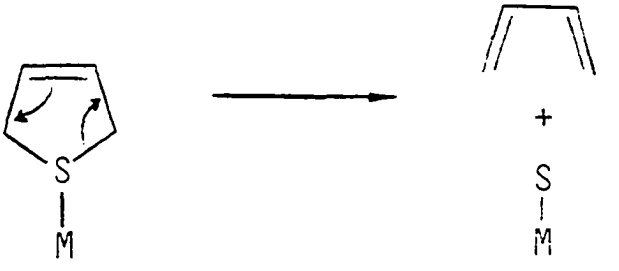
In the reverse coupling reaction, phosphonium ions react with 1,3 butadiene resulting in the formation 3-phospholenium.[13] Both these reactions are proposed to proceed in a concerted fashion.



(3)

$R = N(i\text{-}Pr)_2$

Potentially, once 2,5-DHT is formed over the catalyst, it could readily eliminate butadiene in a similar manner. Thus, if 2,5-DHT is formed from thiophene over the catalyst surface, then the observed



(4)

elimination of butadiene represents a pathway for thiophene HDS. This elimination step has been demonstrated with a transition metal model complex, $Fe(CO)_4$(2,5-DHT), which eliminates butadiene upon thermal

decomposition at 120 °C.[14] Butadiene was also found to be the primary product in the gas phase reaction of 2,5-DHT with hydrogen atoms.[15]

The elimination of butadiene from 2,5-DHT was investigated with reactor studies over $Re/\gamma\text{-}Al_2O_3$ at 300 °C. As with 2,3-DHT, the principal desulfurized product of the reaction of 2,5-DHT was butadiene (64% of the C_4 hydrocarbons), and 1-butene was again observed in thermodynamic excess. It is notable, that 2,5-DHT is substantially more reactive under these conditions than 2,3-DHT. While nearly 40% of the 2,3-DHT remained unreacted, only 13% of the 2,5-DHT was not converted to desulfurized hydrocarbons, Th, THT, or 2,3-DHT. For 2,5-DHT HDS, the formation of large amounts of butadiene is consistent with direct elimination from 2,5-DHT. However, the presence of 2,3-DHT as a product as well, leaves open the possibility that it could be the precursor to the butadiene. Deuterodesulfurization studies at 300 °C over $Re/\gamma\text{-}Al_2O_3$ therefore were undertaken with both 2,3- and 2,5-DHT feeds to investigate further the mechanism for butadiene formation.

Deuterodesulfurization studies. The products of the reaction of 2,5-DHT over $Re/\gamma\text{-}Al_2O_3$ under D_2 at 300° contain surprisingly small amounts of deuterium. Unreacted 2,5-DHT passes over the catalyst nearly unexchanged, 97.6% d_0. The butadiene produced by desulfurization of the 2,5-DHT is 90% d_0 or d_1, as would be expected from direct elimination. The small amounts of deuterium incorporated, (30% d_1), could readily result from exchange of the butadiene after it was formed. Hydrogenation of butadiene over a supported Re catalyst

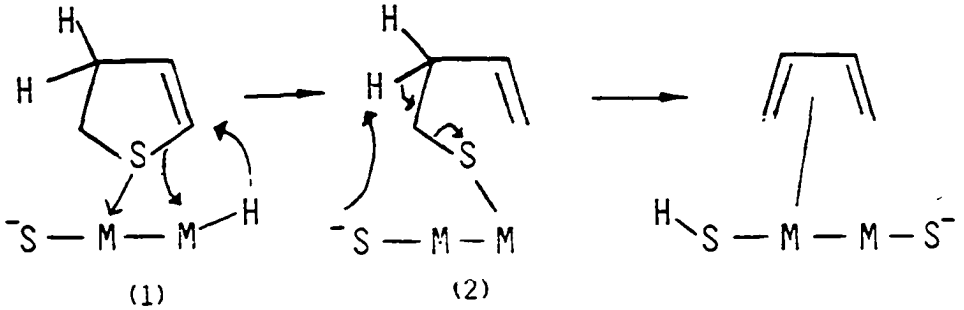
has been examined previously. Deuterium tracer studies showed that of the 10% unhydrogenated butadiene, 40% was either d_1 or d_2.[16]

In contrast, unreacted 2,3-DHT does undergo H-D exchange over the Re catalyst under these conditions. While 30% of the unreacted 2,3-DHT was d_0, 36% was d_1, 20% was d_2, 10% was d_3, and 3% was d_4. ^{1}H NMR shows that ~80% of the deuterium is concentrated in the olefinic positions of the 2,3-DHT, Figure 4.5. Olefinic hydrogens adjacent to sulfur are more acidic than those β to sulfur, being more readily deprotonated by lithium reagents and other strong bases.[17] If exchange over the catalyst involves the initial deprotonation by a surface S^- group followed by deuteration by an SD group, as has been previously suggested for thiophene exchange with D_2 over HDS catalysts,[18] the more acidic a ring hydrogen the more likely it is that exchange will occur. Thus, 2,3-DHT would be expected to incorporate higher amounts of deuterium than 2,5-DHT.

As a result of deuterium incorporation into the 2,3-DHT feed, the HDS products of this reaction have a higher deuterium content. The 2,5-DHT formed from 2,3-DHT isomerization is nearly 45% d_1, d_2, and d_3, but when it was the reactor feed, it was 97.6% d_0. The ^{1}H NMR spectrum of the Th, THT, 2,3-DHT and 2,5-DHT formed from 2,3-DHT DDS shows nearly equal incorporation of deuterium into methylene (α) (10%) and (β) (20%) positions of the 2,5-DHT, Figure 4.5, as would be expected if exchange occurred in the olefinic positions of 2,3-DHT prior to isomerization to 2,5-DHT. Deuterium picked up during isomerization would be at the α position.

Butadiene resulting from desulfurization of 2,3-DHT has a substantially higher deuterium content than that formed from 2,5-DHT desulfurization, with 75% of the product being d_3-d_5 Figure 4.3. Much of this deuterium could have been incorporated through initial deuterium exchange of the 2,3-DHT, thus much of the butadiene could have been formed by the route shown in eqn. 4. Butadiene which is d_5 or d_6, however, probably was not formed from 2,5-DHT by direct elimination. Another pathway for butadiene production from 2,3-DHT could exist. Because nearly 90% of the unreacted 2,3-DHT is d_0, d_1, or d_2, the high amounts of deuterium seen in the product butadiene must be incorporated after an irreversible step, such as C-S bond cleavage. The resultant surface intermediate would undergo exchange, then eliminate butadiene. This first step, C-S bond cleavage, has been observed in transition metal model complexes with π-bound thiophene.[19]

For the complexes [CpRu(η-thiophene)] BF_4, where thiophene is thiophene, 2-methylthiophene, 3-methylthiophene (2- or 3-MT), 2,3-dimethylthiophene (2,3-DMT), 2,3,4-trimethylthiophene (2,3,4-TMT) or 2,3,5,-trimethylthiophene (2,3,5-TMT), attack by hydride results in C-S bond cleavage to give a butadiene thiol. Possibly, a



(5)

similar type of reaction could occur at the olefin in 2,3-DHT, eqn. 5. If hydride attack caused ring cleavage (step 1), the intermediate would still need to be deprotonated (step 2) prior to S elimination to form butadiene as the product. This deprotonation of the less acidic β H's could cause this step to be slow (rate determining), and thus this may allow the intermediate to undergo H-D exchange. Deprotonation and reprotonation with D^+ may be the route for H-D exchange on the catalyst.

The extent to which butadiene is directly formed from 2,3-DHT is not clear, principally because of the higher amount of initial exchange observed for 2,3-DHT. The amount of 2,5-DHT that is formed from the 2,3-DHT and undergoes desulfurization is also not known. Reactor studies however do show that 2,5-DHT is more readily desulfurized than 2,3-DHT, which suggests that thiophene could be hydrogenated to 2,3-DHT which isomerizes to 2,5-DHT which would eliminate S to give butadiene. Alternate pathways where 2,3-DHT undergoes desulfurization to butadiene, or a pathway in which thiophene is directly hydrogenated to 2,5-DHT with elimination of S to give butadiene are also possible. These pathways as well as the interconversions over the catalysts are summarized in Figure 4.8.

As was seen by other researchers in DDS studies with thiophene, the H_2S formed from desulfurization contained no deuterium.[7,9,20] For thiophene, McCarty, and also Cowley have proposed that the H_2S (rather

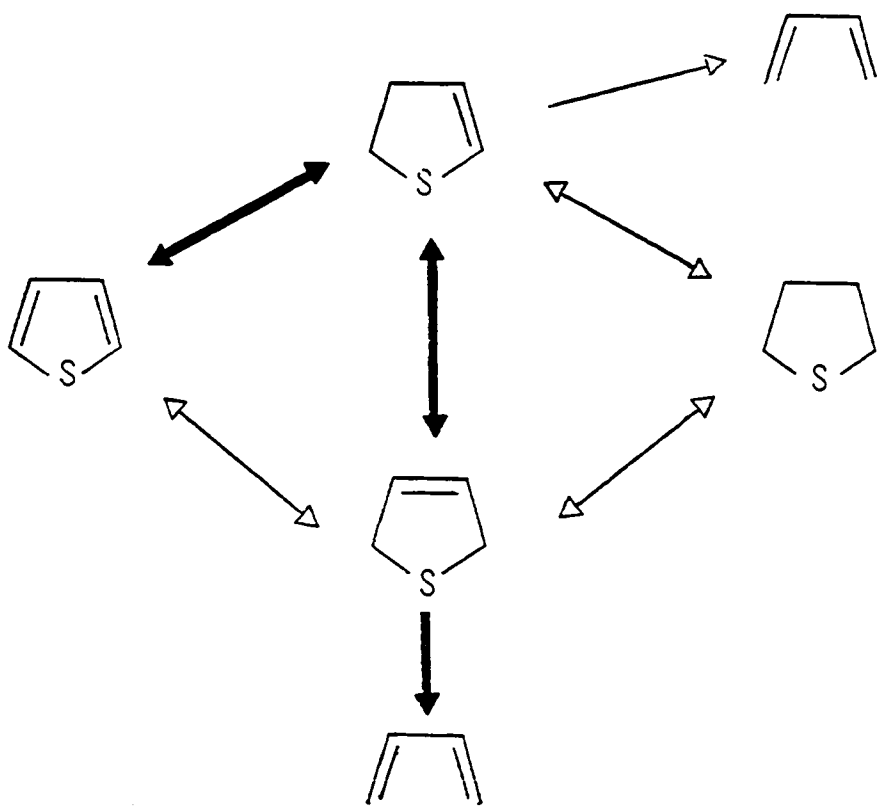


Figure 4.8. Thiophene desulfurization pathways through the dihydrothiophenes to butadiene. The major proposed pathway is shown with bold arrows

than D_2S) is formed because large amounts of hydrogen are exchanged onto the catalyst surface. Cowley observed that while only small amounts of thiophene were desulfurized over a Co-Mo/γAl_2O_3 catalyst, nearly 100% of the α hydrogens of the thiophene feed were exchanged, thus replacing the surface deuterium, leaving the active site enriched in hydrogen (H rather than D). While exchange of the 2,5-DHT and its desulfurization products was not as extensive as for the thiophene, it is quite possible that a surface pool of hydrogen left by exchange is at least in part responsible for the observation of H_2S rather than D_2S. It is likely, however, that in addition to this, a deuterium isotope effect makes the rate of reaction of hydrogen on the catalyst surface faster than that for deuterium, and H_2S is the main product.

Small amounts of deuterium in product tetrahydrothiophene are also seen. Formation of THT from 2,5-DHT or 2,3-DHT under D_2 necessitates the addition of 2 hydrogens (H or D), under D_2, hence, the THT formed should be primarily d_2, or higher. However, for reactions of both 2,5- and 2,3-DHT, the principal THT product was d_0, 52.4 and 39.4% d_0 respectively which could only result if a significant amount of hydrogen were on the surface, or if the rate of transfer of hydrogen from either a M-H or S-H was faster than from M-D or S-D, i.e., a kinetic deuterium isotope effect. Deuterium isotope effects ranging from 2 to 5 have been reported for heterogeneous systems.[22] These studies, however, look at the breaking of C-H bonds, and therefore may not reflect the effects which would be observed over an HDS catalyst. No studies of deuterium isotope effects over

sulfided metal catalysts have been reported in the literature; however, the maximum theoretical kinetic isotope effect for breaking a S-H bond is 5.4, for a metal (M-H) bond, 4.2.[22]

CONCLUSIONS

The high desulfurization activity of 2,3-DHT over Re and Mo/γ-Al_2O_3 catalysts, and the observation that at 300 °C over Re/γ-Al_2O_3 the principle desulfurized product is butadiene support the proposal of 2,3-DHT as an intermediate in the HDS of thiophene. Distributions of the C_4 products from this run indicate that butadiene is hydrogenated to 1-butene which then isomerize to 2-butenes.

Deuterodesulfurization studies show that 2,5-DHT directly eliminates butadiene, and 2,3-DHT can either isomerize to 2,5-DHT, which eliminates butadiene, or cleave a carbon-sulfur bond to eventually give butadiene by a less favorable route.

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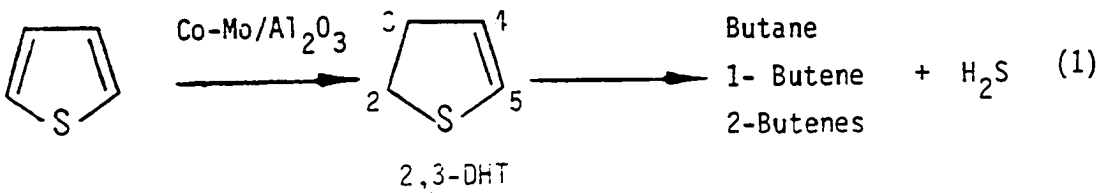
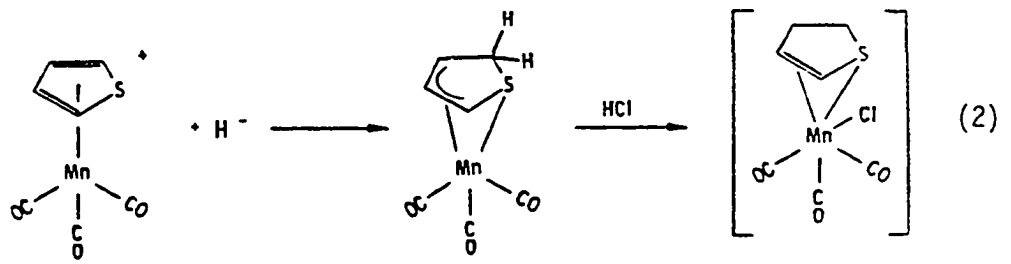
SECTION V. SYNTHESIS, REACTIVITY AND VARIABLE TEMPERATURE NMR STUDIES OF TRANSITION METAL COMPLEXES CONTAINING THE 2,3-DIHYDROTHIOPHENE LIGAND

INTRODUCTION

Hydrogenation of thiophene to 2,3-dihydrothiophene (2,3-DHT), has been proposed as the initial step in the hydrodesulfurization (HDS) of thiophene eqn. 1.[1,2] This is an important step because it converts the aromatic thiophene to the much more reactive 2,3-DHT, which undergoes desulfurization more readily.[3]



Recent model studies of transition metal thiophene complexes suggest a mechanism for the hydrogenation of thiophene to 2,3-DHT at a metal site.[2] Thus, the complex $[Mn(CO)_3(\eta\text{-thiophene})]SO_3CF_3$ undergoes reaction with metal hydrides ($HW(CO)_5^-$ and $HFe(CO)_4^-$) to give an allyl sulfide complex, eqn. 2. Subsequent reaction with HCl, as a model for acidic sites present on the catalyst surface, results in the formation of 2,3-DHT.



In order to understand how 2,3-DHT might be desulfurized to the C_4 products (eqn. 1) on an HDS catalyst we set out to prepare several of its transition metal complexes. Litte is known of the organometallic chemistry of this reactive vinyl thioether, perhaps due to the problems of preparing and purifying the 2,3-DHT, which polymerizes upon warming or in the presence of acids, and decomposes slowly upon exposure to air.[3,4] In addition to the compound prepared by Lesch et al., eqn. 2,[2] only one other complex containing 2,3-DHT as a ligand has been described. Eekhof et al.[5] report the preparation of the S-bound complex $Cr(CO)_5$(2,3-DHT) by photolysis of $Cr(CO)_6$ in a benzene solution containing 2,3-DHT. By preparing transition metal complexes containing 2,3-DHT as a ligand, we sought to establish its preferred binding modes, i.e., via the sulfur, the olefin or both the sulfur and olefin, as well as explore the reactivity of the coordinated ligand from the perspective of modeling HDS reactions. Herein, we describe the facile reaction of 2,3-DHT with transition metal complexes to give S-bound complexes, the reactivity of the coordinated 2,3-DHT ligand, and variable temperature ^1H NMR studies of several 2,3-DHT complexes.

EXPERIMENTAL

General Procedures. All reactions were carried out under N_2 in reagent grade solvents. Methylene chloride and hexanes were dried over CaH_2 and distilled under N_2. Tetrahydrofuran (THF) was distilled from Na-benzophenone under N_2. Pentane and acetone were dried over molecular sieves. All solvents were purged with N_2 prior to use. ^1H NMR and ^{13}C spectra were obtained on a Nicolet NT-300 spectrometer, and variable temperature ^1H NMR studies were done on a Bruker WM-300 spectrometer using deuterated solvents as internal locks. All ^1H NMR chemical shifts are referenced to $(CH_3)_4Si$. ^2H NMR spectra were taken on the Bruker WM-300 spectrometer using the proton signal of the solvent as the internal lock, and $CDCl_3$ at δ 7.26 ppm as the internal reference. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were obtained using a Kratos MS-50 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc. Infrared spectra were obtained using a Perkin-Elmer 681 spectrophotometer and were calibrated using the 1944 cm^{-1} peak of polystyrene. $Re(CO)_5OSO_2CF_3$,[6] $[Ru(CO)_3Cl_2]_2$,[7] K_2PdCl_4,[8] and 2,3-DHT[9] were prepared by literature methods.

Pentane solution of 2,3-DHT. The 2,3-DHT was prepared as described previously.[9] After filtering the 2,3-DHT through the frit covered with Na_2CO_3, the frit was washed 4 times with 25 mL of pentane to give an approximately 0.5 mM solution of 2,3-DHT in pentane

(assuming 100% conversion of 2-acetoxytetrahydrothiophene to 2,3-DHT, and 5% loss of 2,3-DHT during workup). Solutions of 2,3-DHT could be stored in a Dry Ice-isopropanol bath under N_2 for up to 3 weeks. For preparations of the 2,3-DHT metal complexes, 1-3 mL of the pentane solution was used.

Preparation of $W(CO)_5$(2,3-DHT) 1. $W(CO)_6$ (0.500 g, 1.42 mmol) was dissolved in freshly distilled, degassed THF (40 mL) in a quartz photolysis tube equipped with a N_2 bubbler. The resulting solution was photolyzed with a 450 watt, 366 nm lamp for 7 h under N_2 or until no $W(CO)_6$ was apparent by IR. The pentane solution of 2,3-DHT (0.134 g, 1.56 mmol), was added by syringe. The reaction mixture was stirred for 1 h, and the solvent was removed in vacuo. The resulting yellow brown residue was extracted into pentane (3 X 30 mL). The solution was filtered and the pentane removed in vacuo to give a bright yellow powder; yield 0.472 g (1.15 mmol, 81%). Anal. Calcd for $C_9H_6O_5WS$: C, 26.34; H, 1.48. Found: C, 26.18; H, 1.39. ^1H NMR ($CDCl_3$): δ 6.19 (1H, dt, J_{4-5} = 5.70 Hz, J_{3-5} = 2.22 Hz, H_5), 5.87 (1H, dt, J_{3-4} = 2.87 Hz, H_4), 3.53 (2H, t, J_{2-3} = 7.97 Hz, H_2), 2.96 (2H, tt, H_3), ^{13}C NMR (d_8THF): δ 35.4 (C_3), 43.5 (C_2), 127.6 (C_4), 129.6 (C_5), 192.4 (eq CO), 198.0 (ax CO). IR (hexanes): 2070 (w), 1940 (s), 1930 (m) cm^{-1}. EIMS (70 ev)(m/e): M^+(410), M^+-CO (382). M^+-5 CO (270), M^+-2 CO-DHT (268, base peak).

Preparation of $W(CO)_5(THT)$, 2. This compound, 2 was prepared by the same method as 1, from $W(CO)_6$ (0.500 g, 1.42 mmol) and tetrahydrothiophene (THT) (0.125 g, 0.135 mL, 1.51 mmol). It was isolated as a yellow-green powder, yield: (0.509 g (1.24 mmol, 87%). This complex has been previously prepared by Strohmeier, et al.[10] ^1H NMR (CD_2Cl_2): δ 3.91 (2H, m, $H_{2,5}$), 2.07 (2H, m, $H_{3,4}$) ppm. ^{13}C NMR (CD_2Cl_2): δ 31.05 ($C_{3,4}$), 45.37 ($C_{2,5}$) ppm. IR (pentane) 2078 (w), 1939 (s) 1919 (m) cm^{-1}. EIMS (70 eV) (m/e): M^+ (412), M^+-CO (384), M^+-2 CO (256), M^+-3 CO (328).

Preparation of $[Re(CO)_5(2,3\text{-DHT})]SO_3CF_3$, 3. To a solution of $Re(CO)_5OSO_2CF_3$[6] (0.644 g, 1.36 mmol) in acetone (20 mL) was added 2,3-DHT, (0.129 g, 1.50 mmol) in pentane by syringe. After stirring 9 h under N_2, the acetone was removed in vacuo to give a white oil. Prepared in this manner, 3 contained small amounts of impurities. Attempts to recrystallize it however were unsuccessful, and an elemental analysis was not obtained. Yield: 0.641 g (1.14 mmol, 84%). ^1H NMR (d_6-acetone): δ 6.63 (1H, dt, J_{4-5} = 5.67 Hz, J_{3-5} = 2.30 Hz H_5), 6.35 (1H, dt, J_{3-4} = 2.83 Hz H_4), 4.20-4.0 (2H, br, s, H_2), 3.3-3.2 (2H, br, s, H_3). ^{13}C NMR (d_6-acetone): δ 36.00 (C_3) 42.95 (C_2), 123.85 (C_4), 136.23 (C_5), 177.08 (ax CO), 179.38 (eq CO). IR (acetone): 2155 (w), 2057 (s), 2022 (m) cm^{-1}. MS (FAB, glycerol): M^+ (413), M^+-CO (385), M^+-2CO (357), M^+-DHT (327).

Preparation of $PdCl_2(2,3\text{-DHT})_2$, 4. To a slurry of K_2PdCl_4 (0.110 g, 0.337 mmol) in acetone (50 mL) was added 2,3-DHT (0.0585 g, 0.680 mmol) in pentane by syringe. The mixture was allowed to stir 24 h, resulting in a clear reddish-orange solution with no solid K_2PdCl_4 remaining. The acetone was removed in vacuo, and the resultant red-orange solid was recrystallized by dissolving it in a minimum of hot acetone (50 °C) and cooling the solution slowly to -20 °C. Yield: 0.692 g (1.97 mmol, 59%). $C_8H_{12}Cl_2S_2Pd$: C, 27.48; H, 3.46. Found: C, 27.14; H, 3.41. ^1H NMR (d_6-acetone): δ 6.39 (1H, dt, J_{4-5} = 6.0 Hz, J_{3-4} = 2.70 Hz, H_5), 6.24 (1H, dt, J_{3-4} = 2.0 Hz H_4), 2.95 (2H, Br, s, H_2), 2.79 (2H, br, s, H_3). $^{13}C(CDCl_3)$: δ 132.92 (C_5), 122.65 (C_4), 35.60 (C_2), 34.10 (C_3).

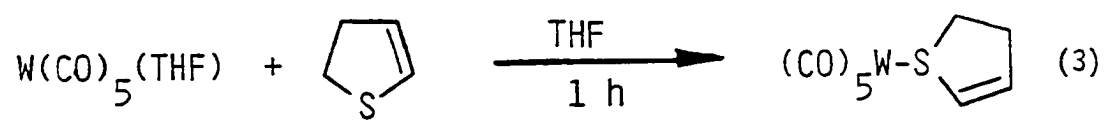
Preparation of $Ru(CO)_3Cl_2(2,3\text{-DHT})$, 5. $[Ru(CO)_3Cl_2]_2$[7] (0.0800 g, 0.156 mmol) was dissolved in 25 mL of dry degassed $CHCl_3$. 2,3-DHT (0.030 g, 0.35 mmole) in pentane was added by syringe, and the mixture was stirred for 4 h. Removal of the solvent in vacuo gave a white powder which was recrystallized from CH_2Cl_2 and hexanes. Yield: 0.078 g (0.114 mmol, 73%). ^1H NMR (CD_2Cl_2): δ 6.39 (1H, dt, J_{4-5} = 5.72 Hz, J_{3-5} = 2.84 Hz, H_5), 6.25 (1H, dt, J_{3-4} = 2.35 Hz, H_4), 4.20 and 3.45 (2H, br, m, H_2), 3.20 and 2.9 (2H, br, m, H_3). ^{13}C (CD_2Cl_2): δ 188.4 (1 CO), 182.1 (2 CO), 136.08 (C_5), 129.71 (C_4), 35.86, 35.65 ($C_{2,3}$). IR ($CHCl_3$) 2138 (s), 2079 (s), 2055 (m) cm^{-1}. EIMS (70 ev) (m/e). M^+ (344), M^+-HCl (306), M^+-2 HCl (270).

Reaction of $W(CO)_5$(2,3 DHT) with HCl. $W(CO)_5$(2,3 DHT) **1** (0.200 g, 0.488 mmol) was dissolved in dry, degassed hexanes (20 mL) in a 50 ml round bottom flask sealed under N_2 with a septum. Gaseous HCl (0.82 mmol), was injected into the solution with a gas tight syringe. The solution was stirred vigorously for 2 h, and the solvent was removed in vacuo. The resultant blue-green solid was extracted with dry degassed pentane giving a green solution, and leaving an insoluble blue solid. The pentane was removed from the solution in vacuo giving a green-yellow powder[3]. Yield 0.0541 g (27%). The ^1H and ^{13}C NMR and mass spectra were the same as those of $W(CO)_5$(THT), 2.

RESULTS AND DISCUSSION

Preparation of Transition Metal Complexes with Sulfur Bound 2,3-DHT. The syntheses described in this section demonstrate that 2,3-DHT forms transition metal complexes by coordinating through its sulfur atom as is typical of simple thioethers.[11] While 2,3-DHT itself is not very stable, polymerizing upon heating and slowly decomposing on exposure to air,[5,10] the complexes **1**, **3**, **4** and **5** containing the S-bound 2,3-DHT are not air or moisture sensitive. They have been stored in air for months without decomposition. In addition, the 2,3-DHT is strongly bound in these complexes. The 2,3-DHT in **1** is displaced only slowly (over 3 h) by a 10 fold excess of t-BuNC. This is in contrast to thiophene, which is aromatic, and coordinates only weakly through its sulfur. Hence, only three complexes of S-bound thiophene have been reported, and in all of them, the thiophene can be readily displaced by weakly coordinating solvents.[12]

Substitution of the labile THF ligand in $W(CO)_5(THF)$ with 2,3-DHT leads to the S-bound 2,3-DHT complex **1**, in high yields, eqn. 3.



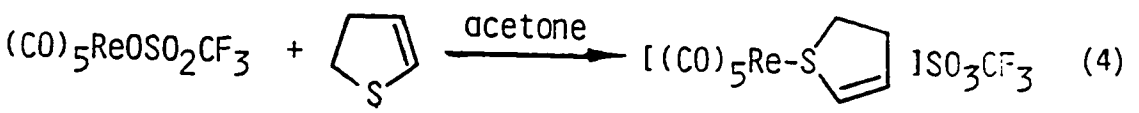
(3)

1

The ^1H and ^{13}C NMR chemical shifts of the 2,3-DHT in **1** support sulfur coordination of the ligand; all resonances are at lower field in the

complexed ligand (^{1}H NMR ($CDCl_3$): δ 6.19, 5.87, 3.53, 2.96 ppm) than in the free ligand (δ 6.14, 5.59, 3.21, 2.74 ppm.)[9] If, on the other hand, olefin coordination had occurred, the olefinic resonances for H_4 and H_5 would be expected to shift to higher field.[13] For example, in $W(CO)_3$(1,6-bis(diphenylphosphino trans hex-3ene), the two olefinic protons shift from 5.5 to 4.34 ppm upon coordination.[13c]

Reaction of 2,3-DHT with $Re(CO)_5OSO_2CF_3$ in acetone leads to substitution of the triflate anion by 2,3-DHT, eqn. 4.



(4)

3

When other less polar solvents such as CH_2Cl_2 or $CHCl_3$ were used for this reaction, 3 did form, but in lower yields. In addition, the time required for reaction was longer and some decomposition of the 2,3-DHT occurred. When the reaction was followed by ^{1}H NMR in d_6 acetone, however, the reaction went cleanly to produce 3. For the reaction in acetone, the solvent was removed giving 3 as a white oil. Attempts to recrystallize 3 from CH_2Cl_2 with nonpolar solvents such as diethylether or hexanes led to decomposition, giving $Re(CO)_5OSO_2CF_3$, and free 2,3-DHT. Because of this, the compound was not obtained analytically pure. 3 was characterized by its IR, ^{1}H and ^{13}C NMR, and FAB mass spectrum.

Reactions of 2,3-DHT with K_2PdCl_4 and $[Ru(CO)_3Cl_2]_2$, which have been shown to react with donor ligands,[14] also give complexes which ^1H NMR indicates that the 2,3-DHT is coordinated only through the S atom. In the Pd(II) salt $[CpPd(PPh_3)(H_2C{=}CH_2)]ClO_4$, the ethylene shifts to higher field by 1.33 ppm when coordinated[15]. Complexes of the formula $[CpRu(PMe_3)_2(acrylonitrile)]BF_4$, have been isolated where the acrylonitrile coordinates either through the nitrogen, or through the olefin. The olefinic hydrogens of the olefin-coordinated isomer are 2.5 ppm upfield from those in the nitrogen-coordinated comples. Since the ^1H NMR olefinic resonances in **4** and **5** shift to higher field rather than lower field, we assign these complexes as S-bound.

$$[Ru(CO)_3Cl_2]_2 + 2 \; \underset{S}{\triangle} \xrightarrow[4\ h]{CHCl_3} 2\ Ru(CO)_3Cl_2(2,3\text{-DHT}) \qquad (5)$$

5

When K_2PdCl_4 was reacted in a 1:1 ratio of Pd: 2,3-DHT, in an attempt to prepare a complex in which both the sulfur and olefin were coordinated, only the bis 2,3-DHT complex, 4, was obtained in 37% yield.

$$K_2PdCl_4 + \underset{S}{\triangle} \xrightarrow[24\ h]{acetone} \begin{matrix} Cl \\ Cl \end{matrix}\!\!>\!Pd\!<\!S \qquad (6)$$

$$\searrow \quad PdCl_2(2,3\text{-DHT})_2$$

4

Reaction with 2 equivalents of 2,3-DHT gave **4** in 60% yield after recrystallization from warm acetone. The product is presumed to have the trans structure as is typical of palladium bisthioethers.[17]

Several other attempts to obtain complexes of S- and olefin-bound 2,3-DHT were also unsuccessive. Photolytic and thermal removal of CO from either **1** or **3**, which would open a site for olefin coordination, led only to decomposition of the complexes. Similarly, when $PdCl_2(2,3\text{-DHT})_2$ was treated with $AgBF_4$, no olefin coordination was observed by ^1H NMR.

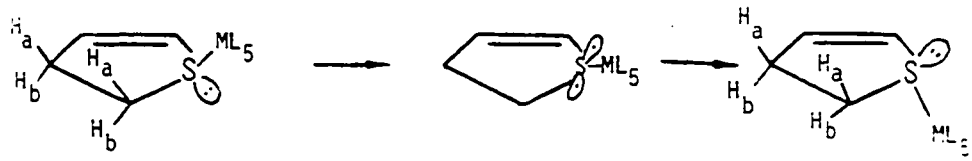
Reactivity of Coordinated 2,3-DHT Complexes. A freshly prepared yellow solution of **1** in $CDCl_3$ turns green within 4 min. Examination of the ^1H NMR spectrum of the solution after approximately 10 min shows two new resonances at δ 3.16 (m) and 2.49 (m) which grow larger as the resonances for the coordinated 2,3-DHT disappear. After 3 hours, a green solid was isolated in relatively low yield (~10%) after evaporation of the solvent and was identified by ^1H and ^{13}C NMR, IR, and mass spectroscopy as $W(CO)_5$(THT) **2**.[10] This complex was also prepared by reaction of $W(CO)_5$(THF) with tetrahydrothiophene, THT. This surprising conversion of coordinated 2,3-DHT to THT was of considerable interest because the hydrogenation of 2,3-DHT to THT is also observed over Re and Mo HDS catalysts supported on γ-Al_2O_3 at 300 °C.[3] Potentially, the conversion of the 2,3-DHT in **1** was initiated by small amounts of HCl present in $CDCl_3$. Indeed, passing the $CDCl_3$ through basic alumina prior to dissolving **1** greatly

decreased the rate of formation of **2**, $W(CO)_5(THT)$. To investigate the possibility that the reaction was initiated by acid, we undertook the reaction of **1** with HCl. When a solution of **1** in hexanes was treated with 1.7 equivalents of HCl, the yellow solution turned green immediately, and **2** was isolated as a yellow-green powder in 27% yield. In an effort to elucidate the route of THT formation, **1** was also reacted with DCl gas in $CDCl_3$.[18] No deuterium incorporation was seen by integration of the ^1H NMR spectrum of **2** at either position of the THT ligand or by ^2H NMR. Therefore, neither HCl nor the solvent $CHCl_3$ is the source of the hydrogen for the formation of the THT ligand. The hydrogen apparently comes from the 2,3-DHT itself. The low yield (27%) of **2** in the reaction of **1** with HCl is consistant with this possibility. None of the other side products of the reaction could be identified.

Another reaction of 2,3-DHT observed over HDS catalysts is dehydrogenation to give thiophene.[4] The mass spectrum of $Ru(CO)_3Cl_2(2,3\text{-DHT})$, **5** shows loss of two HCl from the molecule giving a thiophene-containing fragment, $Ru(CO)_3(thiophene)^+$, presumably containing a thiophene ligand. We sought to promote on a larger scale the elimination of HCl from **5**, giving a thiophene complex, or free thiophene. When **5**, was heated in $CDCl_3$ in an NMR tube for 1 h at 50°, no formation of thiophene or a thiophene-containing complex was observed by ^1H NMR. Likewise, complete thermal decomposition of a small solid sample of **5** at 120 °C in a sealed NMR tube did not result in HCl elimination to give thiophene. Similar reactions were also attempted with $PdCl_2(2,3\text{-DHT})_2$ **4**; however, they again gave no evidence

for the formation of thiophene.

Inversion of Sulfur in Complexes Containing 2,3-DHT. An interesting feature of the 2,3-DHT complexes is the change in their ^1H NMR spectra with temperature. These changes result from the exchange of methylene hydrogens on the same carbon through inversion of the pyramidal sulfur.[19]



(7)

This inversion process, which has been examined in other transition metal-thioether complexes,[19] was conveniently monitored by ^1H NMR for several of the 2,3-DHT complexes. Both the influence of the formal oxidation state of the metal, and the presence of the olefin on the barrier to inversion were examined.[19,20]

The ^1H NMR spectrum of **1**, $W(CO)_5$(2,3-DHT) at room temperature is shown in Figure 5.1. Two resonances are seen for the two sets of methylene hydrogens at δ 3.53 and 2.96 ppm. If no inversion of sulfur was occurring, or if it was very slow on the NMR time scale, four resonances, one for each of the inequivalent methylene hydrogens would be observed. The fact that only one resonance is observed for each set of methylene hydrogens reflects rapid inversion at sulfur on the NMR time scale.[21] In contrast, the room temperature ^1H NMR spectrum

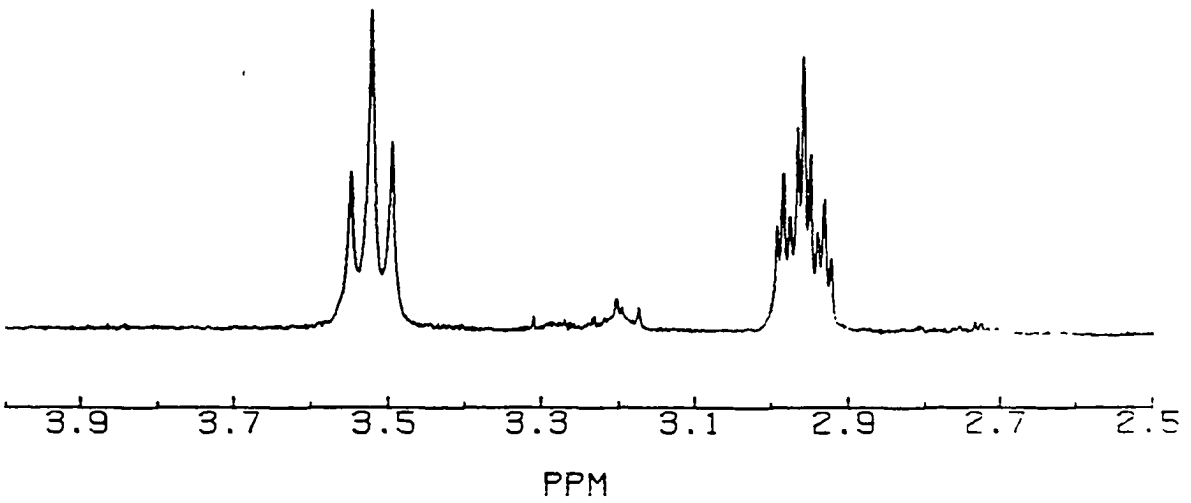


Figure 5.1: Room temperature ^{1}H NMR spectrum of the methylene region of $W(CO)_5$(2,3-DHT), **1** in $CDCl_3$

of **3**, $[Re(CO)_5(2,3\text{-DHT})]SO_3CF_3$, shows two broad signals for the methylene protons. The exchange process is occurring at a rate comparable to that of the NMR time scale. Figure 5.2 shows the room temperature spectrum of **5**, $Ru(CO)_3Cl_2(2,3\text{-DHT})$, where inversion is slow enough that four separate methylene resonances are observed. Based on these qualitative observations, **1**, **3** and **5** follow a trend of increasing barrier to inversion with increasing formal oxidation state of the metal: W(0)<Re(I)<Ru(II). A similar trend was observed previously where the $\Delta G^{\ddagger}$ for inversion was greater for Pt(IV) than Pt(II) in the complexes: $PtXMe(MeSCH_2CH_2SMe)$ vs $PtXMe_3(MeSCH_2CH_2SMe)]$[22], and $PtX_2(MeSCH_2CH_2SMe)$ vs $PtX_4(MeSCH_2CH_2SMe)$.[23]

For **1** and **3**, the barriers to inversion were low enough so that we were able to fully examine the exchange process from the slow to the fast exchange limits. From the coalescence temperature, the barriers to inversion in these complexes were estimated using eqn. 8,[24]

$$\Delta G^{\ddagger} = 1.92\ (T_c)[9.97 + \log(T_c/\delta\nu)] \qquad (8)$$

where T_c is the coalescence temperature, and $\delta\nu$ is the frequency difference in hertz between sites in exchanging system. Coalescence temperatures were determined to ±2 °C, which would give an erro of ±0.5 kJ/mole in $\Delta G^{\ddagger}$.[22] For these systems, $\delta\nu$ was taken simply as the

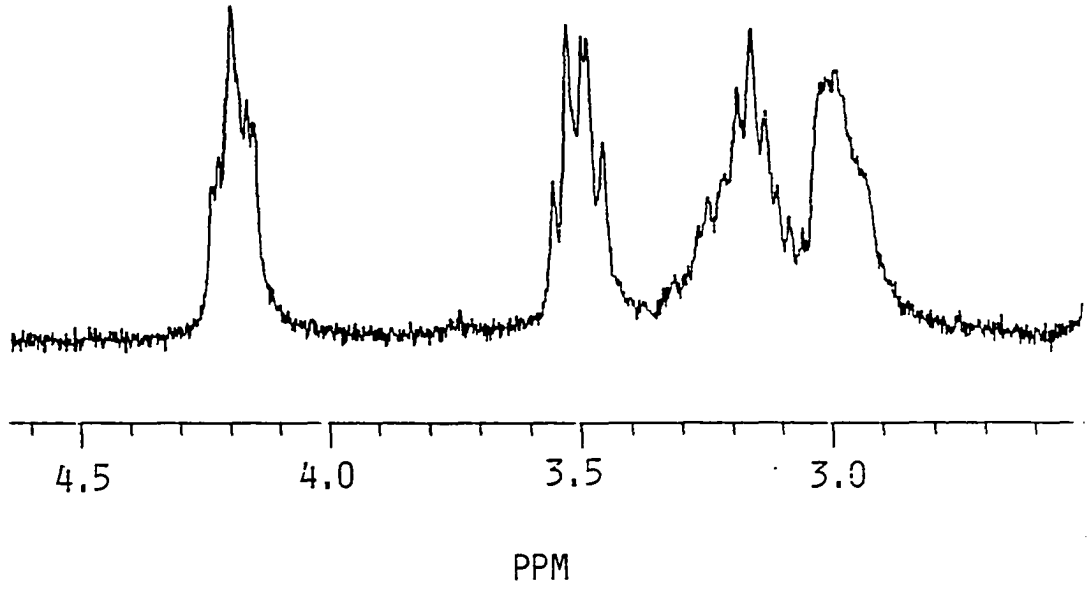
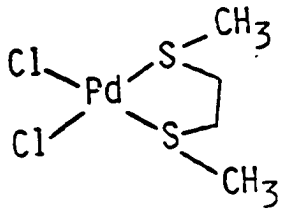


Figure 5.2: Room temperature ^{1}H NMR spectrum of the methylene region of $Ru(CO)_3Cl_2$(2,3-DHT), **5**

separation between the coalescecing multiplets. Using this method, we obtained $\Delta G^{\ddagger}$ values of 48.5 kJ/mol and 62.7 kJ/mol for **1** and **3**, respectively.

While the majority of the Re(I) complexes previously examined have had chelating sulfur ligands, as in $ReCl(CO)_3\{MeS(CH_2)_2SMe\}$, $\Delta G^{\ddagger}$ = 65.1 kJ/mol and $ReI(CO)_3(MeS(CH_2)_2SMe)$, $\Delta G^{\ddagger}$ = 66.7 kJ/mol, the values[25] obtained for inversion are also quite similar to our estimate of 62.7 kJ/mol for **3**. The value obtained for $W(CO)_5$(2,3-DHT) is similar to related complexes, $W(CO)_5(SCH_2SCH_2SCH_2)$, $\Delta G^{\ddagger}$ = 53.0 kJ/mole[26] and $W(CO)_5\{MeSCH_2SCH_2SME\}$, $\Delta G^{\ddagger}$ = 44.5 kJ/mole.[19]

Eekhof et al.[28], reported a value of 45.6 kJ/mol for $W(CO)_5$(2,5-DHT), where 2,5-DHT is the isomer of 2,3-DHT with the double bond between the 3 and 4 carbons. Thus, the inversion barrier for $W(CO)_5$(2,5-DHT) is lower than that (48.5 kJ/mol) for $W(CO)_5$(2,3-DHT), **1** Thus, olefin conjugation with the sulfur in **1** does not lower the inversion barrier. Such a lowering might be expected since the lone pair of electrons on the sulfur in the planar transition state should be stabilized by conjugation with the olefin. This lowering of the inversion barrier conjugation has been observed in a number of transition metal complexes with chelating sulfide ligands e.g.[20,23]:



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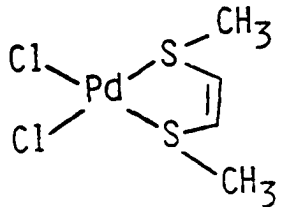
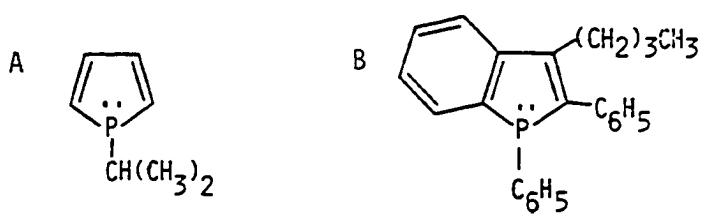
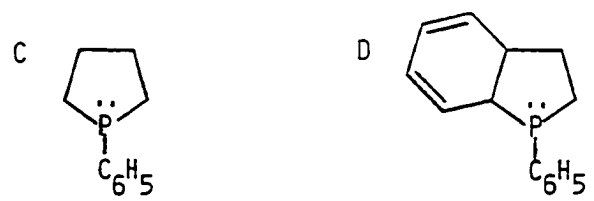


$\Delta G^{\ddagger}$= 81.4 kJ/mol 68.6 kJ/mole

Typically, a decrease in $\Delta G^{\ddagger}$ of 10-12 kJ/mol is observed in conjugated systems. Evidence for π conjugation effects are also seen in inversionn barriers examination of phospholes[29], Figure 5.3. In compounds where the phosphorus lone pair can delocalize in an aromatic ring, inversion barriers are substantially lower than for other systems. The increase in the barrier to inversion in the saturated ring systems (C and D Figure 5.3), reflects the disruption of the "aromaticity" of the phosphole ring. In order to probe further the effect of the olefin bond in **1** and $W(CO)_5$(2,5-DHT) on the inversion barrier, we undertook a variable temperature ^1H NMR study (Figure 3), of **2**, $W(CO)_5$(THT), with the saturated tetrahydrothiophene liquid. The free energy barrier calculated using eqn. 8 is 43.9 kJ/mol. Thus, the trend in inversion barriers for **1**, $W(CO)_5$(2,5-DHT), and **2**, is 48.5, 45.6 and 43.9 kJ/mol, respectively, and can be explained by considering the effect of ring strain. For the series of Pd(II) complexes t-$PdCl_2[S(CH_2)_xCH_2]_2$ where x = 2, 3 or 4, the barrier to inversion increases with increasing ring strain: The decrease in ring size, (i.e. the C-S-C bond angle) presumably constrains access to the planar transition state required for inversion.[20] The ring strain energies for 2,3-DHT, 2,5-DHT, and THT are 18.0, 15.8, and 8.3 kJ/mol,[29] exactly the trend observed for the inversion barriers in the



$\Delta G^{\dagger}$ = 16.1 kcal/mol 23.7 kcal/mol



$\Delta G^{\dagger}$ = 36.5 kcal/mol 35.3 kcal/mol

Figure 5.3: Inversion barriers for P inversion in Phospholes

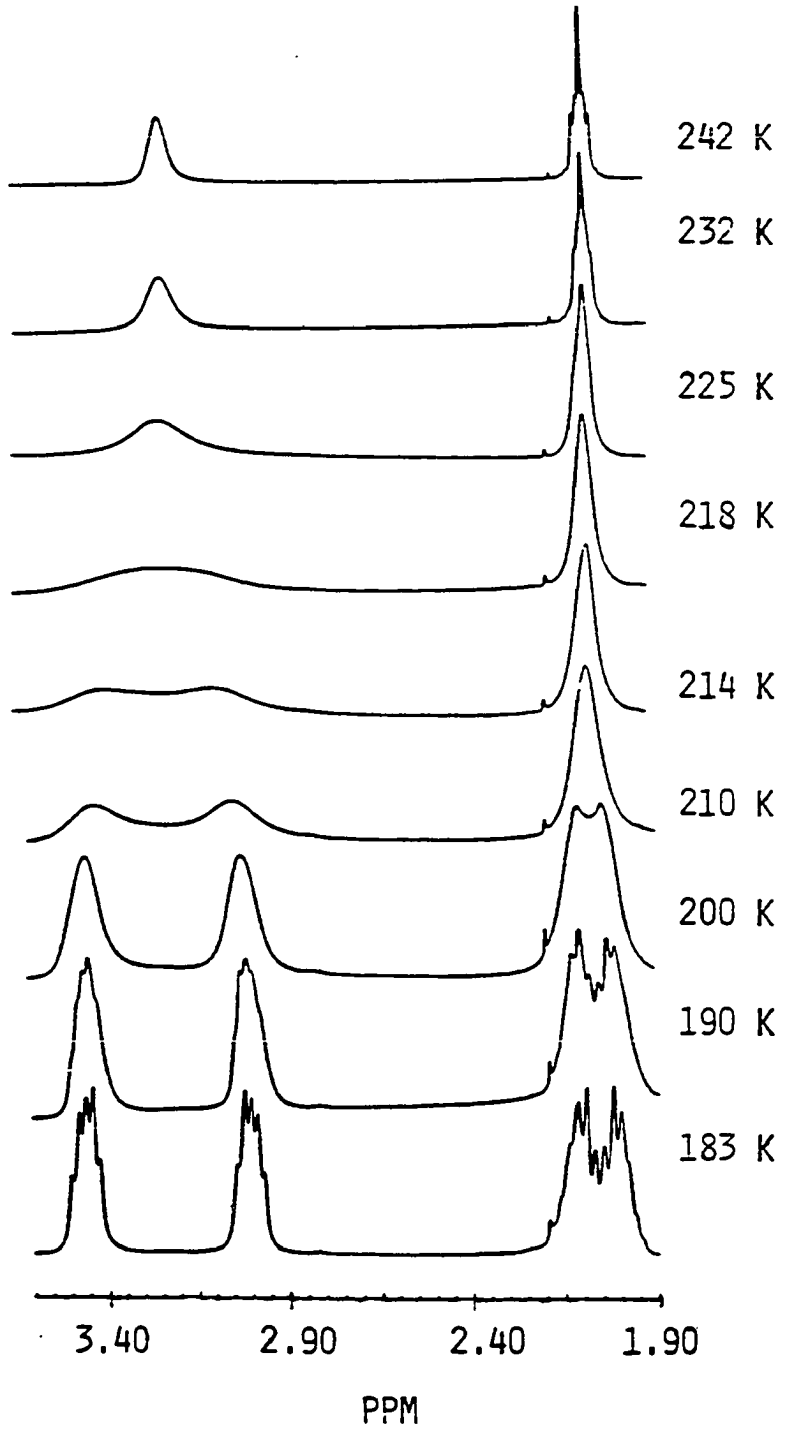


Figure 5.4: Temperature dependent ^{1}H NMR spectrum of $W(CO)_5(THT)$, **2** in $CDCl_3$

analogous complexes. It therefore appears that ring strain is the most important factor determining the rates of inversion of the $W(CO)_5L$ complexes of 2,3-DHT, 2-5-DHT, and THT.

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SUMMARY

The mechanism for catalytic hydrodesulfurization of thiophene is not well understood. We have examined three areas of thiophene HDS, H-D exchange of thiophene over HDS catalysts, the importance of hydrogenated intermediates in thiophene desulfurization, and the desulfurization of proposed these intermediates, using transition metal model complexes, and heterogeneous catalytic reactor studies.

Examination of OH^- promoted deuterium exchange in CD_3OD for the complexes $[CpRu(\eta\text{-th})]^+$ where th = thiophene, 2 or 3 methylthiophene, or 2,5-dimethylthiophene, have demonstrated that π coordination of thiophene on HDS catalyst could be responsible for the observed H-D exchange. The relative rates of exchange of α, β and methyl hydrogens in the model complexes were found to follow the same trend which is observed for heterogeneous exchange, $\alpha > \beta >$ methyl Detailed kinetic studies of the exchange at $H_{3,4}$ show a linear dependence on OH^- consistent with a mechanism where deprotonation of the thiophene occurs in the slow step, followed by deuterium transfer from the solvent CD_3OD.

Reactor studies of 2,3-DHT, 2,5-DHT, and Th, over supported Mo and Re catalysts show that the dihydrothiophenes are much more reactive than thiophene. High conversions to desulfurized products, as well as hydrogenation and dehydrogenation to Th and THT are also seen for both 2,3 and 2,5-DHT. At 300°C, over the Re catalyst, while 2,5-DHT is substantially more reactive than 2,3-DHT, both feeds produce butadiene as the major desulfurized product. The formation of

butadiene is quite significant, as it is frequently proposed as the initial product of thiophene HDS.

Interconversion of 2,3 and 2,5-DHT over the Re catalyst is also seen. This along with the observation that 2,5-DHT is more reactive toward desulfurization suggests that butadiene from 2,3-DHT HDS could result from isomerization of 2,3-DHT to 2,5-DHT with elimination of sulfur to give butadiene. Deuterodesulfurization studies established that while 2,5-DHT directly eliminates butadiene, this pathway is not the only route producing butadiene in 2,3-DHT HDS. The 2,3-DHT is capable of desulfurizing directly to butadiene.

The elimination of butadiene from 2,5-DHT was also seen in the model system $Fe(CO)_4$(2,5-DHT) where the 2,5-DHT is coordinated through its sulfur. While no butadiene was detected in the reaction of 2,3-DHT with $Fe(CO)_4$(THF), isomerization to 2,5-DHT was observed. Conversion of the 2,3-DHT ligand in $(W(CO)_5$(2,3-DHT) to tetrahydrothiophene is catalyzed by H^+. The reactivity of the dihydrothiophenes in these model complexes, and over the HDS catalysts is consistant with their proposed intermediacy in thiophene HDS.

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